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SONIC LINE IN NONEQUILIBRIUM FLOWS

by

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SUMMARY

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An approximate equation valid in the region near the partially frozen sonic line is derived. Solutions of this equation are obtained and it is shown that the curves of constant velocity, the partially frozen sonic line, the line of horizontal velocity and the limiting characteristic are all parabolic. In some cases the sonic line and line of horizontal velocity intersect on either side of the nozzle centerline. It is shown that the line of horizontal velocity lies upstream of the sonic line. Aur HoR

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NOTATION

a	sound speed
A'	expression defined in Eq. (23)
A	expression defined in Eq. (26)
$\mathbf{B}_{\mathfrak{f}}^{\mathfrak{g}}$	expression defined in Eq. (32)
$\mathbf{B}_{\mathbf{f}}$	expression defined in Eq. (34)
С	slope of the velocity along the nozzle axis in the sonic region
g	expression defined in Eq. (65')
901,902	statistical weight of ground energy level for atom and molecule respectively
h	specific enthalpy or Planck constant or nozzle height at throat
k	Boltzmann constant
k _d , k _r	dissociation and recombination rate constants respectively
K _e	equilibrium constant, $\frac{k_d}{k_n}$
K*	expression defined in Eq. (43)
L	expression defined in Eq. (A.5)
m	mass of an atom
ma	mass of atoms per unit mole
M	Mach number; expression defined in Eq. (48)
$\mathbf{M_f}$	frozen Mach number
n	coordinate normal to streamlines
N	expression defined in Eq. (48)
p	pressure
P	expression defined in Eq. (48)

	velocity vector	
	q_x , q_y	x and y components of velocity
	q	speed
	R	gas constant per unit mass referred to diatomic gas
	s	cdordinate along streamlines
4.	t	time
	T	temperature
	x, y	Cartesian coordinates
	x _c , y _c	coordinates of the point where sonic line and line of horizontal velocity intersect
	X*	point where line of horizontal velocity meets nozzle centerline
	\mathbf{x}_{T}	throat location with respect to partially frozen sonic point
	×	degree of dissociation (mass concentration of atom)
	β	defined in Eq. (48), $\frac{K_*}{a_*^*}$
	r_f, r_e	fictitious specific heat ratios for frozen and equilibrium flow respectively (B. 13), (B. 14)
	$\Gamma_{\!f}$, $\Gamma_{\!e}$	true specific heat ratios for frozen and equilibrium flows respectively (A.33), (A.34)
	3	defined in Eq. (23)
	3	constant defined in Eq. (78)
	η	transformed y coordinate
	0	streamline angle
	Θ_{λ} , Θ_{σ} , $\Theta_{\mathfrak{p}}$	characteristic temperatures for rotation, vibration and dis- sociation respectively
	μ	Mach angle
	ξ	transformed x coordinate
	w	expression defined in Eq. (66')

p density

 $\rho_{\mathtt{p}}$ characteristic density for dissociation (A.8)

7 perturbation parameter

 $\mathcal{T}_{\epsilon}, \mathcal{V}_{\epsilon}$ characteristic chemical and flow times

arphi perturbation velocity potential

→ rate parameter (A. 4)

Subscripts:

equilibrium

f = f partially frozen (vibration in equilibrium with active modes; f is used for convenience)

Superscripts:

* reference state

perturbation

1. INTRODUCTION

It is known that in the case of supersonic reacting gas flows in nonequilibrium, the flow field can be calculated by means of the characteristics method with the frozen Mach number playing a role similar to the usual Mach number in non-reacting flows (Refs. 1 to 7). In order to calculate such flows through a nozzle, Der (Ref. 3) has studied the various aspects of the characteristics method for the supersonic part of the nozzle. Similar studies were done by others, for example Ref. 4. However, in all the studies of the nozzle flow, the flow was computed by quasi-one-dimensional methods up to a point where the frozen Mach number is slightly greater than one. The flow properties so obtained are then assumed to be constant along a line perpendicular to the nozzle axis through this point. Using this as the initial data line, the two-dimensional supersonic flow is computed. There appears to be no justification for this assumption of a straight line with constant flow properties as the initial line for the supersonic flow calculations. It therefore appeared worthwhile to investigate the nature of the sonic region (i.e., the region where the frozen Mach number is near unity) so as to establish a correct initial line for the supersonic flow calculations.

In this note it is proposed to study the nature of the sonic region by applying the small perturbation technique. This study may also be useful, at least in a qualitative way, in the transonic region of a reacting flow over a blunt body or in rocket exhaust plumes (Ref. 8).

2. THEORETICAL CONSIDERATIONS

a) Assumptions

(I) The analysis is restricted to the case of a pure diatomic gas like O2, giving a binary mixture of atoms and molecules.

(II) It is assumed that while the vibrational and translational degrees are in equilibrium, dissociation is in nonequilibrium (partially frozen).

(III) It is further assumed, that the dissociation is only slightly out of equilibrium so that the dissociation rate equation may be linearized.

(IV) Only steady flows are considered.

b) Rate equation

The rate equation for the atomic mass fraction α may be written as (Ref. 6, see also the Appendix)

$$\frac{D\alpha}{Dt} = \Psi \cdot L(P, P, \alpha) \tag{1}$$

where $\frac{D}{Dt} = \frac{1}{2}$ grad and ψ is the rate parameter and $L \rightarrow o$ for equilibrium flows.

Consider the flow to be a perturbation from a reference state, which may or may not be in equilibrium, such that

$$P = P^* + P'$$

$$P = P^* + P'$$

$$\alpha = \alpha^* + \alpha'$$
(2)

(where stars denote the reference state and primes the perturbations) and expand L (P, P, X) in a Taylor series about this reference state as

$$L(P,P,\alpha) = L(P,P^*,\alpha^*) + L_{P}P' + L_{P}P' + L_{\alpha}P'$$
(3)

(keeping only the first order quantities). Define a local equilibrium value $\alpha_e = \alpha_e(p,p) = \alpha^2 + \alpha_e'$ such that L $(p,p,\alpha) = 0$. Then expanding L $(p,p,\alpha) = 0$, one has

$$L(p, p, \alpha_0) = L(p^*, p^*, \alpha^*) + L_{p^*}P' + L_{p^*}P' + L_{\alpha}*\alpha_0' = 0$$
 (5)

Thus one can write

$$L(P, P, \alpha) = L_{\alpha*}(\alpha' - \alpha'e) = L_{\alpha*}(\alpha - \alpha_e)$$
 (6)

Now, putting this in the rate equation and writing the rate parameter also as a perturbation from its value for the reference state $\psi = \psi^{+} + \psi'$, and keeping only the first order quantities, one obtains

$$\frac{D\alpha}{Dt} \approx \Psi^* L_{\alpha^*} (\alpha - \alpha_e) \tag{7}$$

c) Basic flow equations

The basic flow equations are

Expanding
$$\frac{DL}{Dt} = h_p \frac{DP}{Dt} + h_p \frac{DP}{Dt} + h_w \frac{DW}{Dt}$$
 (13)

and substituting this in Eq. (10) and using Eqs. (8) and (9),

one obtains

$$-(h_{p}-\frac{1}{p})\rho\vec{q}\cdot\frac{D\vec{q}}{Dt}-\rho h_{p}div\vec{q}+h_{\alpha}\frac{D\alpha}{Dt}=0$$
(14)

where, subscripts denote partial differentiation with respect to that variable. From the definition of frozen speed of sound (Ref. 6)

$$a_{\pm}^{2} = -hp/(h_{p} - 1/p)$$
 (15)

Eq. (14) may be written as

$$\frac{\hbar \alpha}{\rho h_{\rho}} \frac{D\alpha}{Dt} = -\frac{1}{\alpha_{s}^{2}} \vec{q} \cdot \frac{D\vec{q}}{Dt} + d\vec{w} \vec{q}$$
(16)

From the linearized rate equation

$$\frac{D\alpha}{Dt} = \psi_* L_{\alpha^*}(\alpha - \alpha_e) \tag{7}$$

one obtains by differentiation

$$\frac{D}{Dt}\left(\frac{D\alpha}{Dt}\right) = \psi_* L_{\alpha^*}\left(\frac{D\alpha}{Dt} - \frac{D\alpha_e}{Dt}\right) \\
= \psi_* L_{\alpha^*}\left(\frac{D\alpha}{Dt} - \alpha_{ep}\frac{DP}{Dt} - \alpha_{ep}\frac{DP}{Dt}\right) \\
= \frac{\psi_* L_{\alpha^*}}{\lambda_{\alpha}}\left\{P\left(h_p + \lambda_{\alpha}\alpha_{ep}\right)div_{q}q + P\left(h_p + \lambda_{\alpha}\alpha_{ep} - \frac{1}{p}\right)\right\} \frac{Dq}{Dt}\right\} \\
= \psi_* L_{\alpha^*} \frac{P\left(h_p + \lambda_{\alpha}\alpha_{ep}\right)}{h_{\alpha^*}}\left\{div_{q}q - \frac{1}{\alpha_e}q^{\frac{Dq}{Dt}}\right\} \tag{17}$$

where the equilibrium speed of sound a_e is given by (Ref. 6).

$$a_e^2 = -(h_g + h_\alpha \alpha_{ep})/(h_p + h_\alpha \alpha_{ep} - 1/p)$$
 (18)

Eliminating $D_{\overline{L}}^{\underline{c}}$ on the LHS in Eq. (17) by the use of Eq. (16), one finally obtains:

$$\frac{D}{Dt} \left\{ \frac{\rho h_{\rho}}{h_{\alpha}} \left[div \vec{q} - \frac{1}{a_{\uparrow}} \frac{D^{q/2}}{Dt} \right] \right\} = \psi_{\rho} L_{\alpha} + \frac{\rho (h_{\rho} + h_{\alpha} \alpha_{\rho})}{h_{\alpha}} \left[div \vec{q} - \frac{1}{a_{c}} \frac{D^{q/2}}{Dt} \right]$$
(19)

This equation can also be obtained without the assumption of the flow being only slightly out of equilibrium (see Appendix A).

It was shown by Vincenti (Ref. 6) that for flows which are slightly out of equilibrium, one may introduce a velocity potential (see Appendix C). Now writing the velocity as a perturbation from the reference state velocity \boldsymbol{q} *

$$q_x = q'(1 + \varphi_x)$$

$$q_y = q^* \psi_y$$
(20)

where φ is the perturbation velocity potential, and substituting the above in Eq. (19), one obtains

$$\left[(1 + \varphi_{x}) \frac{\partial}{\partial x} + \varphi_{y} \frac{\partial}{\partial y} \right] \left\{ \frac{Ph_{p}}{h_{\alpha}} \left[\varphi_{xx} + \varphi_{yy} - \frac{q^{*2}}{a_{f}} \left[(\psi^{*} + \varphi_{x}) \frac{\partial}{\partial x} + \varphi_{y} \frac{\partial}{\partial y} \right] \left[\frac{(\psi^{*} + \varphi_{x})^{2} + \varphi_{y}^{2}}{2} \right] \right] \right\}$$

$$- \frac{\gamma_{y} L_{\alpha}}{q^{*}} \frac{P(h_{y} + h_{\alpha} \kappa_{ep})}{h_{\alpha}} \left\{ \varphi_{xx} + \varphi_{yy} - \frac{1}{a_{e}^{2}} \left[(\psi^{*} + \varphi_{x}) \frac{\partial}{\partial x} + \varphi_{y}^{2} \right] \left[\frac{(\psi^{*} + \varphi_{x})^{2} + \varphi_{y}^{2}}{2} \right] \right\} = 0(21)$$

d) Relation between sound speed and flow speed:

In order to simplify Eq. (21) for the transonic case, a relation between the sound speeds (frozen and equilibrium) and flow speed is needed. Since the vibrational and translational degrees are assumed to be in equilibrium, the frozen sound speed occurring in the above equation is actually the partially frozen sound speed (in a partially exited dissociating gas) as derived by Glass and Takano (Ref. 5),

$$Q_{\pm}^{2} = \frac{A'+2}{A'}(1+\alpha)RT = \Gamma_{\pm}(1+\alpha)RT \tag{22}$$

where

$$A' = \frac{1}{1+\alpha} \left[5 + \alpha + 2 \left(1 - \alpha \right) \frac{d\xi}{dT} \right]$$

$$\xi = \frac{\theta_v}{e^{\theta_v/T} - 1}$$
(23)

and Risthegasconstant. This expression can be also derived starting from Eq. (15) as shown in the Appendix A

$$A'a_{f}^{2} = (7+3\alpha)RT\left[1 + \frac{2(1-\alpha)}{7+3\alpha}\frac{d\xi}{dT}\right]$$
 (24)

The specific enthalpy may be written as

$$\hat{h} = \frac{7+3\alpha}{2} RT \left[1 + \frac{2(1-\alpha)\xi + 2\alpha \theta_p}{(7+3\alpha)T} \right]$$
 (25)

Using Eq. (24),

$$2h = Aa_f$$

where

$$A = A' \left[1 + \frac{2(1-\alpha)\varepsilon + 2\alpha\theta_0}{(7+3\alpha)T} \right] / \left[1 + \frac{2(1-\alpha)}{7+3\alpha} \frac{d\varepsilon}{dT} \right]$$
 (26)

From Eqs. (9) and (10) for momentum and energy,

$$\frac{D}{D+}(h + \frac{9}{2}) = 0$$

or

$$h + \frac{q^2}{2} = \text{constant} = h_0$$
 (27)

(Since the flow is from a reservoir, $h_{\rm O}$ is the same on all streamlines and hence throughout the flow). Substituting for h from Eq. (26),, one obtains

$$q^2 + A a_f^2 = \text{constant}$$
 (28)

In terms of the critical speed $q * = a_4$ *

$$q^2 + A a_f^2 = (A^* + 1) a_f^{*2}$$
 (29)

or

$$a_{f}^{2} = \left[(A^{*} + 1) a_{f}^{*2} - q^{2} \right] / A$$

$$\simeq \left[(A^{*} + 1) a_{f}^{*2} - q^{2} \right] / A^{*}$$
(30)

Under the assumption of small perturbations A is replaced by A*.

From Ref. 5, the equilibrium speed of sound (see also the Appendix A for derivation from Eq. (18), is given by

$$a_{e}^{2} = \frac{(7+3\alpha)RT}{B_{\frac{1}{2}}} \left[1 + \frac{2(1-\alpha)\frac{d\xi}{d\tau} + \alpha(1-\alpha^{2})(\frac{3}{2} + \frac{B_{0}-\xi}{2})^{2}}{(7+3\alpha)} \right]$$
(31)

where

$$B_{f}' = \frac{2-\alpha}{2} \left[5 + \alpha + 2 \left(1 - \alpha \right) \frac{d\xi}{d\tau} \right] + \alpha \left(1 - \alpha \right) \left(\frac{1}{2} + \frac{Q_{D} - \xi}{T} \right)^{2} \tag{32}$$

Using Eq. (25) for h,

$$2h = B_{t}a_{e}^{2} \tag{33}$$

where

$$B_{f} = B_{f}^{\prime} \left[1 + \frac{2(1-\alpha)\xi + 2\alpha\Omega_{0}}{(7+3\alpha)T} \right] / \left[1 + \frac{1}{7+3\alpha} \left[2(1-\alpha)\frac{d\xi}{dT} + \alpha(1-\alpha^{2})(\frac{3}{2} + \frac{\Omega_{0}-\xi}{T})^{2} \right] \right]$$
(34)

Denoting by a_e^* the value of a_e when $q = a_f^*$, Eqs. (27) and (33) may be combined to give an equation similar to Eq. (29), namely,

$$g^2 + B_f ae^2 = a_f^{*2} + B_f^* ae^{*2}$$
 (35)

$$B_{f} a_{e}^{2} = a_{f}^{*2} - g^{2} + B_{f}^{*} a_{e}^{*2}$$
(36)

Under the assumption of small perturbations, this may be approximated by

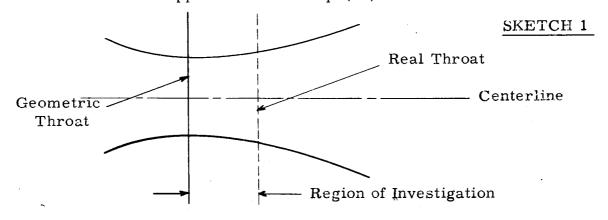
$$a_e^2 \simeq \frac{a_t^{*2} - q^2}{B_t^{*}} + a_e^{*2}$$
 (37)

It may be shown that $B_f \ge A$, $a_j \ge a$, where the equality occurs in the limits $\alpha \to 0$, $\alpha \to 1$.

It is shown in the Appendix A that the errors introduced in replacing A by A* and B; by B_{\ddagger} * in deriving Eqs. (30) and (37) from Eqs. (29) and (36) are not large.

3. TRANSONIC APPROXIMATION

As noted previously the purpose of this note is to study the flow field in the sonic region in a nozzle for flows which are slightly out of equilibrium. For such flows it can be shown from a quasi-one-dimensional analysis that the sonic point occurs a short distance downstream of the geometrical throat. Clarke (Ref. 9) has also shown that, in nonequilibrium flows, the flow speed at the geometrical throat is always equal to the equilibrium sound speed at that point. It can also be shown that in the case of frozen or equilibrium flows, the sonic point is again at the geometrical throat. It is also known that the frozen and equilibrium sound speeds at any point in a nonequilibrium flow may differ up to 15%. Noting these comments, one may derive the transonic approximation of Eq. (21) as follows.



To determine the order of the various terms in Eq. (21), consider new variables ξ , η , $\overline{\phi}$ (ξ , η) given by.

$$\overline{\varphi}(x,y) = \Upsilon h. \overline{\varphi}(\xi,\eta)$$
 (38)

and
$$\xi = x/h_o$$
, $\eta = \gamma^{1/2}y/h_o$, $q^* = a_f^*$

where h_0 is the semi-height of the nozzle at the throat and $\overline{\phi}$, $\partial/\partial\xi$, $\partial/\partial\eta$ are of order unity (see Appendix C for details about this transformation) Also from Appendix C

$$\frac{\varrho h_{\ell}}{h_{\alpha}} = \frac{\varrho_{*} h_{\varrho^{*}}}{h_{\alpha^{*}}} \left(1 + T R_{i}^{\prime} \right) \tag{38'}$$

and

$$\frac{\rho(h_{\ell} + h_{\alpha} \alpha_{e\ell})}{h_{\alpha}} = \frac{\rho_* (h_{\ell}^* + h_{\alpha^*} \alpha_{e\ell}^*)}{h_{\alpha^*}} (1 + \gamma R_2')$$

where R'_1 and R'_2 are given in Eqs. (C19) and (C.21) of Appendix C.

Transforming Eq. (21) to the new variables by the transformation of Eq. (38), substituting for $\frac{\theta_e}{h_a}$ and $\frac{\theta_e}{h_a} = \frac{\theta_e}{h_a}$, one obtains

$$\begin{split} &\left[\left(1+\Upsilon\bar{\varphi}_{\underline{e}}\right)\frac{\partial}{\partial\underline{e}}+\Upsilon^{2}\bar{\varphi}_{\underline{m}}\frac{\partial}{\partial\overline{\eta}}\right]\left(1+\Upsilon R'_{1}\right)\left\{\Upsilon\bar{\varphi}_{\underline{e}}\left[1-\left(\frac{\alpha_{\underline{e}}^{*}}{\alpha_{\underline{e}}}\right)^{2}\left(1+\Upsilon\bar{\varphi}_{\underline{e}}\right)^{2}\right]\right.\\ &\left.+\Upsilon^{2}\bar{\varphi}_{\eta\eta}\left(1-\Upsilon^{3}\frac{\alpha_{\underline{e}}^{*2}}{\alpha_{\underline{e}}^{2}}\bar{\varphi}_{\eta}^{2}\right)-2\Upsilon^{3}\left(\frac{\alpha_{\underline{e}}^{*}}{\alpha_{\underline{e}}}\right)^{2}\bar{\varphi}_{\eta}\bar{\varphi}_{\underline{e}}\eta\left(1+\Upsilon\bar{\varphi}_{\underline{e}}\right)\right\}-\frac{h_{0}\Psi_{\underline{e}}L_{\alpha_{\underline{e}}}\left(h_{\underline{e}}+h_{\alpha_{\underline{e}}}\alpha_{\underline{e}}\underline{e}\right)}{\alpha_{\underline{e}}^{*}h_{\underline{e}}^{*}}\left(\frac{1+\Upsilon\bar{\varphi}_{\underline{e}}}{\alpha_{\underline{e}}}\right)^{2}-\frac{h_{0}\Psi_{\underline{e}}L_{\alpha_{\underline{e}}}\left(h_{\underline{e}}+h_{\alpha_{\underline{e}}}\alpha_{\underline{e}}\underline{e}\right)}{\alpha_{\underline{e}}^{*}h_{\underline{e}}^{*}}\left(\frac{1+\Upsilon\bar{\varphi}_{\underline{e}}}{\alpha_{\underline{e}}}\right)^{2}+\Upsilon^{2}\bar{\varphi}_{\eta\eta}\left(1-\Upsilon^{3}\frac{\alpha_{\underline{e}}^{*2}}{\alpha_{\underline{e}}^{*}}\bar{\varphi}_{\eta}^{2}\right)-2\Upsilon^{3}\left(\frac{\alpha_{\underline{e}}^{*}}{\alpha_{\underline{e}}}\right)^{2}\bar{\varphi}_{\eta}\bar{\varphi}_{\underline{e}}\eta\left(1+\Upsilon\bar{\varphi}_{\underline{e}}\right)^{2}=0\end{split}$$

One can further show by the use of Eqs. (30) and (37) that

$$1 - \left(\frac{O_{\pm}^{*}}{O_{+}}\right)^{2} \left(1 + \Upsilon \overline{\varphi}_{E}\right)^{2} = -2 \Upsilon \overline{\varphi}_{E} \left(\frac{A^{*} + 1}{A^{*}}\right) + O(\Upsilon^{2}) \tag{40}$$

and

$$1 - \left(\frac{\alpha_{e}^{*}}{\alpha_{e}}\right)^{2} \left(1 + \gamma \overline{\varphi_{e}}\right)^{2} = 1 - \left(\frac{\alpha_{e}^{*}}{\alpha_{e}^{*}}\right)^{2} \overline{\varphi_{e}} \left(1 + \frac{\alpha_{e}^{*2}}{\beta^{*} \alpha_{e}^{*2}}\right) + o(\gamma^{2})$$

$$(41)$$

So that Eq. (39) finally reduces to

$$\begin{split} &\left[\left(1+\Upsilon\bar{\varphi}_{\underline{e}}\right)\frac{\partial}{\partial \underline{e}}+\Upsilon^{2}\bar{\varphi}_{\underline{m}}\frac{\partial}{\partial m}\right]\left(1+\Upsilon R_{1}^{\prime}\right)\left\{-p\Upsilon^{2}\bar{\varphi}_{\underline{e}}\bar{\varphi}_{\underline{e}}+\Upsilon^{2}\bar{\varphi}_{\underline{m}}+O(\Upsilon^{3})\right\}\\ &-h_{o}\beta\left(1+\Upsilon R_{2}^{\prime}\right)\left\{\Upsilon M\bar{\varphi}_{\underline{e}}-\Upsilon^{2}N\bar{\varphi}_{\underline{e}}\bar{\varphi}_{\underline{e}}+\Upsilon^{2}\bar{\varphi}_{\underline{m}}+O(\Upsilon^{3})\right\}=0 \end{split} \tag{42}$$

where

$$P = 2 (A^{*} + 1)/A^{*}$$

$$M = 1 - \alpha_{f}^{*2}/\alpha_{e}^{*2}$$

$$N = \frac{2 \alpha_{f}^{*2}}{\alpha_{e}^{*2}} \left(1 + \frac{\alpha_{f}^{*2}}{\beta_{f}^{*} \alpha_{e}^{*2}}\right)$$

$$\beta = \frac{K_{*}}{\alpha_{f}^{*}}$$

$$K_{*} = \Psi_{*} L_{*} + (h_{e}^{*} + h_{d}^{*} \alpha_{e}^{*2})/h_{e}^{*}$$
(43)

If one keeps only terms of the lowest order in Eq. (42), one has the trivial case $\overline{\varphi}_{\xi\xi} = 0$ or $\overline{\varphi}_{\xi} = f(\gamma)$. Thus to the next higher order (i. e. Υ^2), one has

$$\Upsilon^{2} \frac{\partial}{\partial E} \left\{ - P \overline{\Psi}_{E} \overline{\Psi}_{EE} + \overline{\Psi}_{TT} \right\} - h_{o} \beta \left\{ \Upsilon M \overline{\Psi}_{EE} - \Upsilon^{2} N \overline{\Psi}_{E} \overline{\Psi}_{EF} + \Upsilon^{2} \overline{\Psi}_{TT} \right\} = 0$$
 (44)

Transforming back to the original variables $oldsymbol{\phi}$, $\,$ x , $\,$ y,

$$\frac{\partial}{\partial x} \left\{ - p \, \mathcal{L}_x \, \mathcal{L}_{xx} + \mathcal{L}_{yy} \right\} - \beta \left\{ M \, \mathcal{L}_{xx} - N \, \mathcal{L}_x \, \mathcal{L}_{xx} + \mathcal{L}_{yy} \right\} = 0 \tag{45}$$

The parameter $\beta = K*/a_f^*$ in this equation tends to infinity to the limit of equilibrium flow. Thus small deviations from equilibrium for which this equation is derived, imply very large but finite values of β . Hence the limit of frozen flow given by $\beta \rightarrow 0$ cannot be logically derived from this equation. However, it will be seen that, by putting $\beta = 0$ in Eq. (45), one obtains a transonic equation valid for frozen flows. This result can be considered only fortuitous. Hereafter the limit of frozen flow will not be considered.

3.1 Equilibrium Flow:-

In this limit $\beta \rightarrow -\alpha$ and hence Eq. (45) simplifies to

$$\varphi_{xx} \left[1 - \frac{\alpha_{t}^{*2}}{\alpha_{e}^{*2}} - \frac{2\alpha_{t}^{*2}\varphi_{x}}{\alpha_{e}^{*2}} \left(1 + \frac{\alpha_{t}^{*2}}{\beta_{t}^{*}\alpha_{e}^{*2}} \right) \right] + \varphi_{yy} = 0$$
(46)

Referring the perturbation to the equilibrium critical speed of sound a_e^* (i.e. when $a_e = q = a_e^*$) and writing $q = a_e^* (\mu \varphi_e)$, a_f^* in Eq. (46) is to be replaced by a_e^* , thus,

$$-2\frac{B_{e}^{*}+1}{B_{e}^{*}}\varphi_{x}'\varphi_{xx}'+\varphi_{yy}'=0$$
 (47)

where B_e^* is now the value for $a_e = g = a_e^*$.

3.2 Solutions for the nozzle flows:-

To study the flow in the sonic region, one has to solve the following equation,

$$\frac{\partial}{\partial x} \left\{ -P \Psi_x \Psi_{xx} + \Psi_{yy} \right\} - \beta \left[M \Psi_{xx} - N \Psi_x \Psi_{xx} + \Psi_{yy} \right] = 0 \tag{45}$$

where

where
$$P = z \frac{A^* + 1}{A^*}$$

$$\beta = \frac{K_*}{a_*^*}$$

$$M = 1 - \frac{a_*^* z^*}{a_*^*} (1 + \frac{a_*^* z^*}{a_*^*})$$
In the case of a nozzle symmetric with respect to the centerline(i.e., z -axis)

the γ -component of the velocity is antisymmetric in γ while the z -component is symmetric. Also for supersonic flow, the perturbation component \mathscr{C}_{\varkappa} changes from negative to positive values as one passes through the sonic line. Thus the perturbation velocity potential may be written as

$$\Psi(x,y) = \varphi_0(x) + \frac{y^2}{2} \varphi_1(x) + \frac{y^4}{24} \varphi_2(x) - \cdots$$

where $\psi_o(x)$ gives the potential on the z axis (i.e., y=0). By substituting this in the above equation, one can solve for the functions ψ_i, φ_i -- etc. in terms

$$\begin{aligned} & \mathcal{L}_{x} = \mathcal{L}_{0x} + \frac{y^{2}}{2} \mathcal{L}_{1x} + \frac{y^{4}}{24} \mathcal{L}_{2x} \\ & \mathcal{L}_{xx} = \mathcal{L}_{0x} + \frac{y^{2}}{2} \mathcal{L}_{1xx} + \frac{y^{4}}{24} \mathcal{L}_{2xx} \\ & \mathcal{L}_{xx} = \mathcal{L}_{0x} \mathcal{L}_{0xx} + \frac{y^{2}}{2} (\mathcal{L}_{0x} \mathcal{L}_{1xx} + \mathcal{L}_{1x} \mathcal{L}_{0xx}) + \frac{y^{4}}{24} (\mathcal{L}_{0x} \mathcal{L}_{1xx} + \mathcal{L}_{0x} \mathcal{L}_{2xx} + \mathcal{L}_{3x} \mathcal{L}_{0xx}) + \cdots \\ & \mathcal{L}_{yy} = \mathcal{L}_{1}(x) + \frac{y^{2}}{2} \mathcal{L}_{2}(x) \end{aligned}$$

which gives for φ

$$\frac{\partial \Psi_{i}}{\partial x} - \beta \Psi_{i} = (-\beta N + P \frac{\partial}{\partial x})(\Psi_{ox} \Psi_{oxx}) + \beta M \Psi_{oxx}$$

$$e^{-\beta x} \Psi_{i} = \int e^{-\beta x} (-\beta N + P \frac{\partial}{\partial x})(\Psi_{ox} \Psi_{oxx}) dx + \int \beta M e^{-\beta x} \Psi_{oxx} dx + \text{constant}$$

$$\Psi_{i}(x) = e^{\beta x} \left\{ \int e^{-\beta x} \left[(-\beta N + P \frac{\partial}{\partial x})(\Psi_{ox} \Psi_{oxx}) + \beta M \Psi_{oxx} \right] dx + A \right\}$$
(49)

where A is an integration constant.

In the region near the throat, one may write, (as in perfect gas flows, see Ref. 10),

 $\varphi_{ox} = C \chi$ where c is a positive constant found by taking the origin of the axes $\chi = \psi = 0$ at the sonic point. Substituting for φ_{ox} , φ_{oxx} in Eq. (49), one obtains,

$$\varphi_{l}(x) = \left\{ \frac{(N-P)C^{2}}{\beta} - MC + NC^{2}x \right\} + Ae^{\beta x}$$
(50)

The equation for $\Psi_{\lambda}(x)$ is

$$\frac{\partial \mathcal{Y}_{2}}{\partial x} - \beta \mathcal{Y}_{2} = (-\beta N + P \frac{\partial}{\partial x})(\mathcal{Y}_{0x}\mathcal{Y}_{1xx} + \mathcal{Y}_{1x}\mathcal{Y}_{0xx}) + \beta M\mathcal{Y}_{1xx}$$

$$\mathcal{Y}_{2} = e^{\beta x} \left\{ \int e^{-\beta x} \left[(-\beta N + P \frac{\partial}{\partial x})(\mathcal{Y}_{0x}\mathcal{Y}_{1xx} + \mathcal{Y}_{1x}\mathcal{Y}_{0xx}) + \beta M\mathcal{Y}_{ux} \right] dx + B \right\}_{(51)}$$

where B is an integration constant.

Substituting for $\varphi_{0x}, \varphi_{0xx}, \varphi_{1x}, \varphi_{1xx}$, one has

$$f_2(x) = N^2 c^3 + A \beta^2 x e^{\beta x} \left[\frac{\beta c x}{z} (P - N) + ((zP - N) + \beta M) + B e^{\beta x} \right]$$
 (52)

Thus the perturbation velocity potential $\mathcal{Y}(x,y)$ and the x, y components of the perturbation velocity \mathcal{V}_x , \mathcal{V}_y are:

$$\varphi(x,y) = \frac{cx^{2}}{2} + \frac{y^{2}(N-P)c^{2}}{2} - Mc + Nc^{2}x + Ae^{Ay} + \frac{y^{4}}{24} \left[N^{2}c^{3} + A\beta^{2}x e^{Ay} \frac{Bcx}{2}(P-N) + c(2P-N) + BM\right] + Be^{Bx}$$
(53)

$$\varphi_{x} = C\chi + \frac{y^{2}}{2}(NC^{2} + A\beta e^{\beta x}) + \frac{y^{4}}{24} \left\{ A\beta^{3}C(P-N)\chi e^{\beta x} + A\beta^{3}\chi e^{\beta x} \left[\frac{\beta C\chi}{2}(P-N) + \beta M \right] + B\beta e^{\beta x} \right\}$$
(54)

$$\varphi_{y} = y \left\{ \frac{(N-P)c^{2}}{\beta} - Mc + Nc^{2}x + A e^{\beta x} + \frac{y^{2}}{6} \left[N^{2}c^{3} + A\beta^{2}x e^{\beta x} \left[\beta \frac{Cx}{2} (P-N) + C(2P-N) + \beta M \right] + Be^{\beta x} \right] \right\}$$
(55)

3.2.1 Limiting case of equilibrium flow:

In this limit $\beta \rightarrow -\infty$, and replacing \mathcal{A}^* by \mathcal{A}^*_e as in Section 3.1, $M = O(N) = \frac{2(\beta_e^* + 1)}{\beta_e^* + 1}$ where β_e^* is the value at the point where equilibrium critical speed is obtained. Thus the components of the velocity are:

$$\Psi_{x} = c \times + \frac{Be^{*} + I}{Be^{*}} c^{2} y^{2}$$

$$\tag{56}$$

$$4y = \frac{2(Be^{2}+1)}{Be^{2}} c^{2}y \left\{ x + \frac{cy^{2}}{3} \frac{Be^{2}+1}{Be^{2}} \right\}$$
 (57)

Equation (56) shows that the constant perturbation velocity curves Ψ_{\star} are parabolas.

The sonic line and the line of horizontal velocities are obtained by putting $\varphi_x = \varphi_y = 0$, respectively,

Sonic line is
$$\chi + \frac{B_e^* + 1}{B_e^*} C y^* = 0$$
 (58)

Line of horizontal velocity is
$$\chi + \frac{\beta_c^* + 1}{\beta_c^*} \frac{cy^2}{3} = 0$$
 (59)

Both lines are parabolas and have the common point x=y=0, as in perfect gas flows. (See Appendix B)

3.2.2 General nonequilibrium case:-

The (x, y)-components of the perturbation velocity for the general nonequilibrium case are,

$$Y_{y} = y \left\{ \frac{(N-P)C^{2}}{\beta} - MC + \frac{NC^{2}}{\delta} x + Ae^{\beta x} + \frac{y^{2}}{\delta} \left(N^{2}C^{3} + A\beta^{2}xe^{\beta x} (\beta C \frac{x}{\delta} (P-N) + C(2P-N) + (55) \right) \right\}$$

$$\beta M) + Be^{\beta x}$$

As noted previously, β is negative and very large for small deviations from equilibrium (see also Appendix). So, all the exponential and other terms in β in Eqs. (54) and (55) may be neglected giving the approximate results

$$\Psi_{X} = C\left(X + \frac{NCY^{2}}{Z}\right) \tag{54}$$

$$4y = Nc^{2}y(x - \frac{M}{NC} + \frac{Ncy^{2}}{6})$$
 (55)

These results could have been obtained as well by neglecting the contribution of the first term in Eq. (45).

Eq. (54) shows that the curves of constant velocity $f \simeq a_f^* + \varphi_x$ are parabolic. Thus the initial data curve for supersonic flow calculations by the method of characteristics can be taken as a parabolic arc with constant flow properties on this curve.

The frozen sonic line and the line of horizontal velocity are given by $\psi_x = \psi_{\psi} = 0$ respectively.

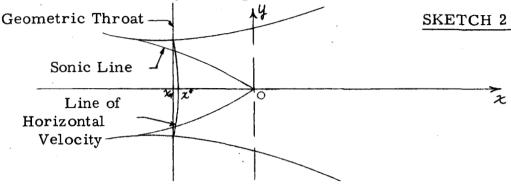
Sonic Line:
$$O = x + NCy^2/2$$
 (56)

Line of Horizontal Velocity
$$O = \mathcal{V} - \frac{M}{NC} + \frac{Ncy^2}{6}$$
 (57)

Eqs. (56), (57) show that these two curves do not meet on the axis as in perfect gas flows (See Appendix B). The point where the line of horizontal velocity meets the x axis i. e. y = 0 is obtained by putting y = 0 in Eq. (57),

$$\chi^* = \frac{M}{NC} \tag{58}$$

Since $\ell_1^* > \ell_e^*$, M < 0. Also N > 0. Thus χ^* is upstream of the sonic point. In other words, the line of horizontal velocity intersects the x axis upstream of the sonic line. This is physically sound since, one should have parallel flow in the vicinity of the geometric throat



This displacement of the sonic point from the geometric throat can be obtained by using the boundary condition on the nozzle wall that $\Psi_y = 0$ when the wall is parallel to the centerline or x-axis. If χ_{τ} is the abscissa of the throat and h the throat height, then

$$0 = \chi_T - \frac{M}{NC} + \frac{NCh^2}{6}$$

$$\chi_T = \frac{M}{NC} - \frac{NCh^2}{6}$$
(59)

If the sonic line and line of horizontal velocity cross, this crossover point is given by the solution of Eqs. (56), (57) for x, y. This point is

$$\chi_{c} = \frac{3}{2} \frac{M}{NC}$$

$$y_{c} = \frac{\sqrt{-3M}}{NC}$$
(60)

 $y_c = \sqrt{-3M}$ This crossover occurs only if $y_c = y_w$ (x = x_c), where $y_w = y_w$ (x) is the wall equation.

Other limiting cases:- Two other limiting cases can be considered where the amount of dissociation α tends to 0 or 1 and correspondingly $\beta \to \infty$. In these cases $\alpha_f \xrightarrow{*} \alpha_e \xrightarrow{*} \alpha^*$ and $\beta_f \xrightarrow{*} A^*$

$$\Psi_{x} = c \times + \frac{A^{*} + 1}{A^{*}} c^{2} y^{*} \tag{61}$$

and

$$4y = 2 \frac{A^{*}+1}{A^{*}} c^{2} y \left\{ x + \frac{Cy^{2}}{3} \frac{A^{*}+1}{A^{*}} \right\}$$
 (62)

Thus the sonic line is

$$O = \chi + \frac{A^* + I}{A^*} C y^2 \tag{63}$$

Line of horizontal velocity is

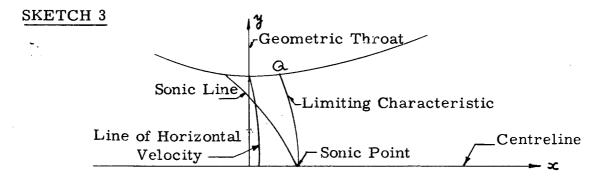
$$O = \chi + \frac{A^* + I}{A^*} \frac{c y^2}{3} \tag{64}$$

both of which are parabolas and have the common point x = y = 0.

4. CHARACTERISTICS

to

The flow through a nozzle can be divided into two distinct parts: (i) the subsonic region and that part of the supersonic region which influences the subsonic part, (ii) the remainder of the supersonic field. Consider a point Q on the nozzle wall, such that the frozen Mach line emanating from it meets the sonic line on the nozzle centerline. Mach lines coming from all points upstream of Q will reflect on the sonic line and thus influence the subsonic and transonic part of the flow. Thus the knowledge of the location of the limiting Mach lines and the point Q will be of interest in the nozzle flows, particularly, for the inverse nozzle problem.



In the perfect gas case, it is known that the point Q lies upstream of the throat (Ref. 10). In this section, the situation in the reacting gas flows will be considered.

4.1 Characteristics for Near-Equilibrium Flow

In section 2.c., the basic system of Eqs. (7) to (12) was reduced

$$\operatorname{div} \vec{q} - \frac{1}{a_f^*} \vec{q} \cdot \frac{D\vec{q}}{Dt} = \frac{h_{\alpha}}{\rho h_{\rho}} \frac{D\alpha}{Dt}$$
 (16)

$$\frac{D\alpha}{Dt} = \psi_* L_{\alpha^*}(\alpha - \alpha_e) \tag{7}$$

In terms of streamline coordinates s, n, these may be written as

$$(M_f^2 - 1)\frac{\partial g}{\partial s} - g\frac{\partial o}{\partial n} + g = 0 \tag{65}$$

$$9\frac{\partial\alpha}{\partial s} = \varpi \tag{66}$$

where $M_f = \frac{9}{a_f}$ the frozen Mach number,

$$g = h\alpha/\rho h\rho$$
 (65')

$$\overline{\omega} = \psi_* |_{\mathcal{U}} (\alpha - \alpha_e) \tag{66'}$$

For small deviations from equilibrium, Vincenti (Ref. 6) has shown that the flow may be considered irrotational, thus

$$\frac{\partial \mathcal{P}}{\partial n} - \mathcal{P} \frac{\partial \theta}{\partial s} = 0 \tag{67}$$

Eq. (66) is already in characteristic form, the characteristics being streamlines. For the system of Eqs. (65), (67), the characteristic directions ℓ_1 , ℓ_2 can be shown to be given by

$$\left(\frac{ds}{dn}\right)_{\ell_1,\ell_2} = \pm \sqrt{M_{\pm}^2 - 1}$$
 (68)

and the compatibility relations along these characteristics are

$$\mp \sqrt{M_{1}^{2}-1} dq + q d0 \mp \frac{q}{M_{1}} dl_{1,2} = 0$$
 (69)

4.1.1 Approximation in the Sonic Region

In Eq. (40), the approximate value of $M_{\xi}^2 - 1$ is derived for the sonic region, and is given by

$$\mathsf{M}_{\downarrow}^{2} - 1 \simeq \frac{2 \left(A^{*} + 1 \right)}{A^{*} \mathcal{O}_{\downarrow}^{*}} \, \mathcal{V}_{\times} \tag{70}$$

neglecting higher order terms. If μ is the frozen Mach angle i.e. $\sin \mu = \frac{1}{M_P}$, then

$$\cot \mu = \sqrt{M_f^2 - 1}$$

$$\simeq \left[P \Psi_x \right]^{\frac{1}{2}} \tag{71}$$

where P is given in Eq. (48).

The approximate form of the compatibility relation valid in the sonic region is obtained by replacing q by $a_{\sharp}^* + q' \simeq a_{\sharp}^* + q' \simeq a_{\sharp}^* + q' \simeq a_{\sharp}^* + a_{\sharp}^* = a_{\sharp}^* +$

$$\mp \left[P_{4x}\right]^{k} \frac{dq}{dl} + d0 \mp \frac{\hbar \alpha}{\rho h}, \frac{\varpi}{M_{f}} dl_{1,2} = 0 \tag{72}$$

In Cartesian coordinates \mathbf{z}, \mathbf{y} the characteristic directions are given as

$$\frac{dy}{dx} = \tan(0 \pm \mu) \tag{73}$$

In the sonic region, which is in the vicinity of the geometric throat, if the nozzle contour is sufficiently smooth and slowly varying, θ will be small compared to μ which is nearly $\pi/2$ and hence one may approximate for the characteristic directions in Cartesian coordinates

$$\frac{dy}{dx} \approx \pm \tan \mu \approx \pm (P \varphi_x)^{1/2} \tag{74}$$

4.1.2 Limiting Characteristics

By use of the solution Ψ_{x} given in Eq. (54) or (54), one can

find the characteristic curves in the sonic region by integrating Eq. (70). As this integration is a little complicated, restricting our attention to the limiting characteristics i.e. those passing through the origin x=y=0, consider if any parabolas

$$\frac{2}{y^2} = 5 \tag{75}$$

can coincide with the characteristics. The slope of the parabola is

$$\frac{dx}{dy} = 25y \tag{76}$$

Substituting in Eq. (70) and using Eq. (54') for Ψ_{κ} , one finds

$$45^2 = (C5 + \frac{NC^2}{2})P \tag{77}$$

OT

$$S = \frac{Pc \pm \sqrt{P^{2}c^{2} + 8PNc^{2}}}{8} = \frac{Pc}{8}(1 \pm \sqrt{1 + \frac{8N}{P}})$$
 (78)

Since M and P are positive, ζ is real and is positive or negative according to the sign between the root and hence the limiting characteristics are parabolic.

The point Q on the wall (where the limiting characteristic emanates) can be obtained by solving the wall equation

$$y_{w} = y_{w}(x) \tag{79}$$

and the left running characteristic equation

$$\frac{\mathcal{X}}{\mathbf{y}} = \frac{PC}{8} \left(1 - \sqrt{1 + \frac{gN}{P}} \right) \tag{80}$$

5. SPECIFIC CALCULATIONS

As an illustration, the flow of pure dissociated oxygen through

a hyperbolic nozzle for reservoir conditions $T_o = 5900$ Kand $P_o = 82$ atm. is calculated for which quasi-one dimensional results were available (although this example is drawn from a completely nonequilibrium case, it serves the purpose, since in the throat region T_v and T_t differ only slightly and is equivalent to the partially excited model). The values of T_v^* , α^* were taken from the quasi-one dimensional results, from which the parameters in Ψ_x , Ψ_y were calculated and found to be

A'* = 3.905,
$$a_{\tilde{f}}^*$$
 = 1.494, $B_{\tilde{f}}^{!*}$ = 31.218, $a_{\tilde{e}}^*$ = 1.340, A* = 9.487, $B_{\tilde{f}}^*$ = 11.783, P = 1.4797, M = -0.242, N = 1.8378.

The equation of the hyperbolic nozzle was

$$4/h = 1 + (x/.38)^2$$

where the origin of the coordinate axes are now taken at the geometric throat for convenience. The variation of the perturbation velocity $\mathcal{G}_{\kappa} \approx \mathcal{G}_{\kappa} \approx \mathcal{G$

$$Y_x = 3.285 (x + 6.037 y^2/z)$$

 $Y_y = 19.832 (x + 0.04 + 6.037 y^2/6)$

 $\psi_{x} = \psi_{y} = 0$ giving the sonic line and line of horizontal velocity respectively. The limiting characteristics were found to be

$$\frac{x}{y^2} = -1.308$$

 $\frac{x}{y^2} = 2.523$

The displacement of the frozen sonic point from the geometric throat and the point where the line of horizontal velocity meets the centerline were found to be

$$\chi_{\tau/h} = -0.85$$

 $\chi^*/h = -0.8$

respectively. The point where the sonic line and line of horizontal velocity cross is found to be

$$\chi_{c/A} = -1.2$$

 $\chi_{c/A} = \pm 2.82$

The limiting characteristics, frozen sonic line and the line of horizontal velocity are shown in Fig. 2.

6. DISCUSSION

One important objection that may be raised about the analysis of Section 3 concerns the linearization of the rate equation while keeping terms of order Υ^2 in the approximation for the potential equation. If the variation of α in the sonic region is much smaller than the variation of γ , one may feel justified in the linearization of rate equation. The results of quasi-one dimensional calculation for two cases, where the flow is slightly out of equilibrium ($\frac{\alpha-\alpha_0}{\alpha}\approx 8\%$), showed that, in the sonic region, α varied by 0.3% while γ varied by 3% from the critical state values. Thus the linearization of the rate equation appears justified.

This analysis will give at least a qualitative description of the flow, if not a quantitative one, and is carried out in the same spirit as that of Vincenti (Ref. 11). It may be noted that it gives the correct trends in the prediction of the sonic line downstream of the gometric throat and the line of horizontal velocity in the vicinity of the geometric throat. Since the curves of constant velocity are shown to be parabolic, the calculation of the supersonic flow field by the method of characteristics can be started from an initial data curve which is the arc of a parabola or a circle. The values of the various flow variables, obtained by quasi-one dimensional analysis, may be taken constant along this curve.

A similar analysis can be done if one considers nonequilibrium in a single mode (e.g. vibrational nonequilibrium with no dissociation). In that case the rate equation has to be replaced by the Landau-Teller equation for vibrational nonequilibrium.

It was found from some preliminary analysis that the case of simultaneous vibrational and dissociational nonequilibrium cannot be reduced to a single equation as in the present case regardless of whether one considers coupled or uncoupled models for the vibrational and dissociational rate processes.

7. CONCLUSIONS

The qualitative picture one obtains for the nozzle flow in nonequilibrium is:

- i) The lines of constant velocity are parabolic.
- ii) The frozen sonic line is parabolic and displaced downstream

of the geometric throat.

- iii) The line of horizontal velocity is parabolic and meets the nozzle centerline upstream of the frozen sonic line.
- iv) The frozen sonic line and the line of horizontal velocity meet on either side of the nozzle centerline, in case $M \approx O$ (i.e. $\mathcal{Q}_{1}^{1} \approx \mathcal{Q}_{e}^{2}$) or do not meet at all as in the example given, in contrast to the perfect gas flows where they meet on the nozzle centerline. In the earlier case portions of the horizontal velocity curve near the nozzle walls will be supersonic while those near the centerline will be subsonic or in the latter case the whole curve is subsonic in contrast with the perfect gas flows where the whole curve is supersonic.
- v) The limiting characteristic which divides the nozzle flow into two distinct regions, (namely, I. the subsonic flow and that part of the supersonic flow which influences the subsonic flow, and II. the fully supersonic flow) is parabolic and emanates from a point on the nozzle wall which is downstream of the geometric throat in contrast to perfect gas flows where it is upstream of the geometric throat.
- vi) The initial data curve for the computation of the supersonic flow by the method of characteristics may be taken as a parabolic or circular arc with constant flow properties on it which may be obtained from quasi-one-dimensional calculations.
- vii) It appears from a rough analysis given in Appendix A that the qualitative picture for simultaneous nonequilibrium in vibration and dissociation may be similar to the present case. However, the partially frozen speed of sound used in the present analysis is to be replaced by the fully frozen speed of sound.

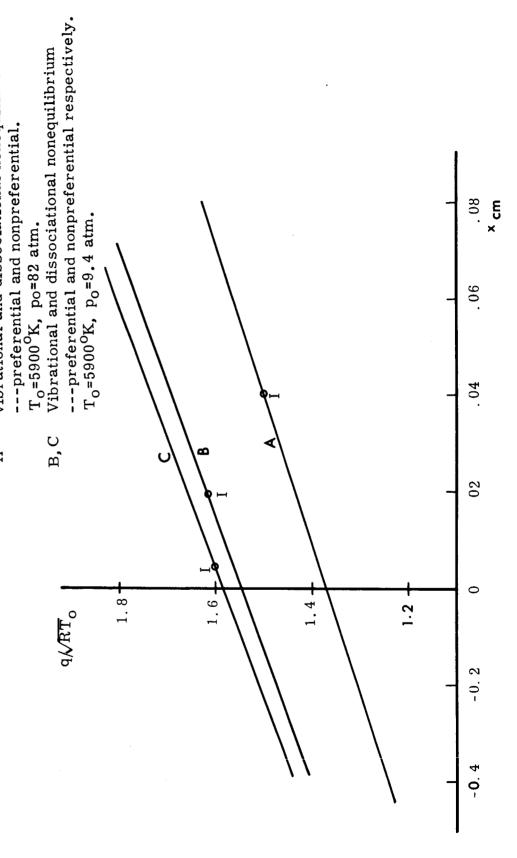
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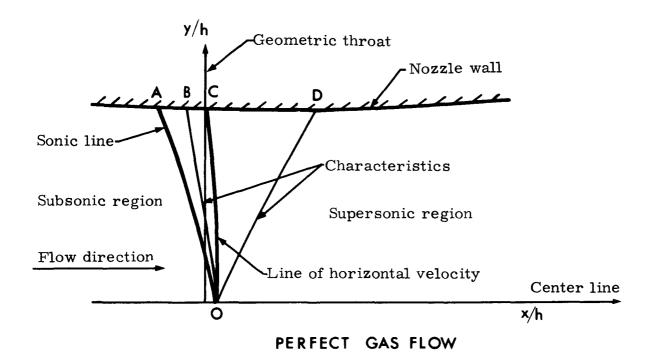
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Figure 1. Variation of q Along the Nozzle Axis. (quasi-one dimensional calculation)
Hyperbolic nozzle.

vibrational and dissociational nonequilibrium

point where q = a_f





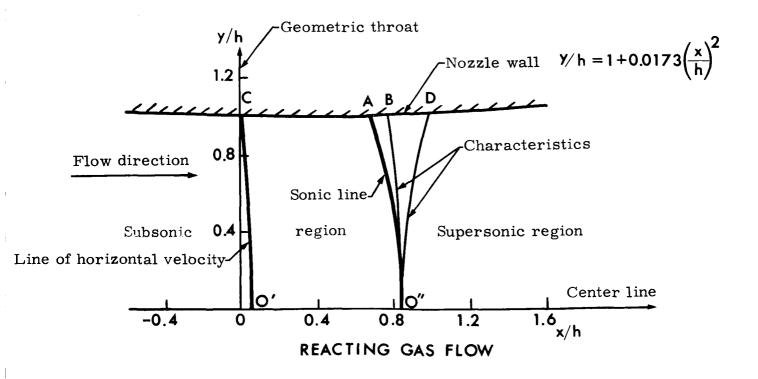


Figure 2

NOZZLE TRANSONIC FLOW REGION IN A PERFECT GAS AND IN A DISSOCIATED OXYGEN FLOW $p_0=82atm., T_0=5900^{O}K, \checkmark_0=0.69$

APPENDIX A

DERIVATIONS

Rate Equation

It was shown in Ref. 5 that for dissociation and recombination of a pure diatomic gas described by the process

$$A_2 + X \xrightarrow{k_1} 2A + X \tag{A.1}$$

where A_2 and A are a diatomic molecule and an atom, respectively, and X is a third body, k_d , k_h are the dissociation and recombination rate constants respectively, the rate equation for the net production of atoms in terms of the atomic mass fraction α , may be written as

$$\frac{D\alpha}{Dt} = \frac{k_{\rm A} \, l^2 (1+\alpha) \alpha^2}{m_a^2} \left[\frac{m_a}{2\rho} \, k_c \frac{(1-\alpha)}{\alpha^2} - 1 \right] \tag{A.2}$$

where M_a is the mass of atoms per unit mole, ρ is the density and K_c is the equilibrium constant defined by

$$K_c = \frac{k_d}{k_h} \tag{A.3}$$

In this derivation the atoms and molecules are considered to have the same efficiency in causing dissociation. If they are considered to have different efficiencies, then the factor ($1+\alpha$) in Eq. (A.2) has to be replaced by ($1-\alpha+2\lambda\alpha$) where λ is the relative efficiency of atoms and molecules. Comparing Eq. (A.2) with Eq. (1) in the text, one finds

$$\psi = k_{\Lambda} \int_{-\infty}^{\infty} (1+\alpha) \alpha^{2} / m_{\alpha}^{2} \qquad (A.4)$$

and

$$L(p, p, \alpha) = \frac{m_a}{2p} K_c \frac{(l-\alpha)}{\alpha^2} - 1 \tag{A.5}$$

It may be noted that L is dimensionless and $/\psi$ has the dimensions of time and is taken as the characteristic chemical time γ_{ϵ} . If γ_{f} is the characteristic flow time, then for $\gamma_{f} \to 0$, one obtains the limit of equilibrium flow and for $\gamma_{f} \to \infty$, the limit of frozen flow. Also in the limit of equilibrium flow $L \to 0$, giving the equation for the equilibrium mass fraction of atoms as

$$\frac{d_e^2}{1-\alpha_e} = \frac{m_a \kappa_c}{2\beta} \qquad (A.6)$$

In Ref. 5, an expression for K_c is obtained from thermodynamics

as
$$K_c = \frac{4f_b}{m_a} \left(\frac{T}{Q_{11}}\right)^{1/2} \left(1 - e^{-Q_{11}/T}\right) e^{-Q_{21}/T}$$
 (A.7)

where θ_h , θ_v , θ_D are characteristic temperatures for rotation, vibration and dissociation respectively, m is the mass of an atom, k, h are Boltzmann and Planck constants, g_{o_1} , g_{o_2} are statistical weights of the ground energy level for atoms and molecules respectively.

Expressions for K*, ae, af

Now expressions for these parameters explicitly in terms of the state variables P, P, \propto , \top will be derived. In this Appendix, the function L is obtained in terms of P, T, \propto whereas in the main text, it was in terms of P, P, \propto .

Using the equation of state

$$p = \rho R T (1 + \alpha) \tag{A.9}$$

one can write

$$L(p, T, \alpha) = L[T(p, p, \alpha), p, \alpha] = L(p, p, \alpha) \quad (A. 10)$$

$$\begin{split} dL &= (L_{\alpha})_{p,T} d\alpha + (L_{p})_{T,\alpha} d\beta + (L_{T})_{p,\alpha} dT \\ &= L_{\alpha} d\alpha + L_{p} d\beta + L_{T} [(T_{p})_{p,\alpha} d\beta + (T_{p})_{p,\alpha} d\beta + (T_{\alpha})_{p,p} d\alpha] \\ &= [(L_{\alpha})_{p,T} + (L_{T})_{p,\alpha} (T_{\alpha})_{p,p}] d\alpha + [(L_{p})_{T,\alpha} + (L_{T})_{p,\alpha} (T_{p})_{p,\alpha}] d\beta + (L_{T})_{p,\alpha} (T_{p})_{p,\alpha} d\beta \\ &= (L_{\alpha})_{p,p} d\alpha + (L_{p})_{p,\alpha} d\beta + (L_{p})_{p,\alpha} d\beta & (A.11) \end{split}$$

$$(L_{\alpha})_{\beta,\rho} = (L_{\alpha})_{\rho,\tau} + (L_{\tau})_{\rho,\alpha} (T_{\alpha})_{\beta,\rho} .$$
 (A. 12)

From Eq. (A. 9)

$$(\mathsf{T}_{\alpha})_{\mathfrak{p},p} = -\frac{\mathsf{T}}{l+\alpha} \tag{A. 13}$$

From Eqs. (A. 5) and (A. 7)
$$(L_{\kappa})_{\rho,\tau} = -\frac{m_{\ell}}{2 \rho} K_{\ell} \frac{2-\kappa}{\kappa^{3}}$$
 (A. 14)

$$(L_T)_{\rho,\alpha} = \frac{m_a}{e\rho} \frac{(1-\alpha)}{\alpha^2} \frac{K_c}{T} \left(\frac{1}{\alpha} + \frac{Q_0 - \mathcal{E}}{T}\right) \tag{A.15}$$

Thus

$$(L_{\alpha})_{p,p} = -\frac{m_{\alpha} k_{c}}{2 p} \frac{2-\alpha}{\alpha^{2}} - \frac{T}{1+\alpha} \frac{m_{\alpha}}{2 p} \frac{1-\alpha}{\alpha^{2}} \frac{k_{c}}{T} \left(\frac{1}{2} + \frac{g_{b}-\xi}{T}\right)$$

$$= -\frac{m_{\alpha} k_{c}}{2 p} \frac{1-\alpha}{\alpha^{2} (1+\alpha)} \left(\frac{4+3\alpha(1-\alpha)}{2\alpha(1-\alpha)} + \frac{g_{b}-\xi}{T}\right) \quad (A. 16)$$

$$\psi(L_{x})_{p,p} = -k_{d} \frac{f(1-x)}{2m_{a}} \left[\frac{2}{x(1-x)} + \frac{3}{2} + \frac{g_{b}-\xi}{T} \right]$$
 (A. 17)

The enthalpy h is

$$h(T,\alpha) = \frac{7+3\alpha}{2}RT + (I-\alpha)RE + \alpha RO_{p}$$
 (A. 18)

$$h(T,\alpha) = h[T(P,P,\alpha),\alpha] = h(P,P,\alpha)$$

$$dh = (h_T)_{\alpha} dT + (h_{\alpha})_{\tau} d\alpha$$

$$= (h_T)_{\alpha} [(T_P)_{P,\alpha} dP + (T_P)_{P,\alpha} dP + (T_{\alpha})_{P,P} d\alpha] + (h_{\alpha})_{\tau} d\alpha$$

$$= (h_T)_{\alpha} [(T_P)_{P,\alpha} dP + (h_T)_{\alpha} [T_P)_{P,\alpha} dP + [(h_T)_{\alpha} [T_{\alpha})_{P,P} + (h_{\alpha})_{\tau}] d\alpha$$

$$= (h_P)_{P,\alpha} dP + (h_P)_{P,\alpha} dP + (h_{\alpha})_{P,P} d\alpha$$

$$= (h_P)_{P,\alpha} dP + (h_P)_{P,\alpha} dP + (h_{\alpha})_{P,P} d\alpha$$

$$(A. 20)$$

Similarly the local equilibrium mass fraction of atoms α_e is

where
$$\alpha_e(\rho, T)$$
 is given by Eq. (A.6) and

$$d \propto_{e} = (\alpha_{ep})_{\tau} d\rho + (\alpha_{e\tau})_{\rho} d\tau$$

$$= (\alpha_{ep})_{\tau} d\rho + (\alpha_{e\tau})_{\rho} [(T_{p})_{p,\alpha_{e}} d\rho + (T_{p})_{p,\alpha_{e}} d\rho + (T_{\alpha_{e}})_{p,\rho} d\alpha_{e}]$$

$$d \propto_{e} [1 - (\alpha_{e\tau})_{\rho} (T_{\alpha_{e}})_{p,\rho}] = [(\alpha_{ep})_{\tau} + (\alpha_{e\tau})_{\rho} (T_{p})_{p,\alpha_{e}} d\rho + (\alpha_{e\tau})_{\rho} (T_{p})_{p,\alpha_{e}} d\rho$$

$$d \propto_{e} = \frac{[(\alpha_{ep})_{\tau} + (\alpha_{e\tau})_{\rho} (T_{p})_{p,\alpha_{e}}] d\rho + (\alpha_{e\tau})_{\rho} (T_{p})_{p,\alpha_{e}} d\rho}{[1 - (\alpha_{e\tau})_{\rho} (T_{\alpha_{e}})_{p,\rho}]}$$

$$= (\alpha_{ep})_{p} d\rho + (\alpha_{e\tau})_{\rho} d\rho$$

$$(A. 22)$$

Thus from Eqs. (A.20) and (A.22)

$$\frac{h_{\rho} + h_{\alpha} \propto_{ep}}{h_{\rho}} = \frac{(h_{\tau})_{\alpha} T_{\rho})_{p,\alpha} [1 - (\alpha e \tau)_{\rho} (T_{\alpha} e)_{p,\beta}] + [(h_{\tau})_{\alpha} (T_{\alpha})_{p,\rho} + (h_{\alpha})_{\tau}] [(\alpha e \rho)_{\tau} + (\alpha e \tau)_{\rho} (T_{\rho})_{p,\alpha} e]}{(H_{\tau})_{\alpha} (T_{\rho})_{p,\alpha} [1 - (\alpha e \tau)_{\rho} (T_{\alpha} e)_{p,\rho}]}$$

$$= \frac{(h_{\tau})_{\alpha} [(T_{\rho})_{p,\alpha} + (T_{\alpha})_{p,\rho} (\alpha e \rho)_{\tau}] + (h_{\alpha})_{\tau} [(\alpha e \rho)_{\tau} + (\alpha e \tau)_{\rho} (T_{\rho})_{p,\alpha} e]}{(h_{\tau})_{\alpha} (T_{\rho})_{p,\alpha} [1 - (\alpha e \tau)_{\rho} (T_{\alpha} e)_{p,\rho}]} (A. 23)$$

From Eqs. (A.6), (A.7), (A.9), (A.18)

$$(\alpha_{e\tau})_{\rho} = \frac{\alpha_{e}(1-\alpha_{e})}{(2-\alpha_{e})T} \left(\frac{1}{2} + \frac{\theta_{b}-\varepsilon}{T}\right) \tag{A.24}$$

$$(\alpha_{ep})_{T} = -\frac{\alpha_{e}(1-\alpha_{e})}{P(2-\alpha_{e})} \tag{A.25}$$

$$(T_{\kappa})_{p,\ell} = -T/1+\alpha \tag{A. 26}$$

$$(T_p)_{p,\alpha} = -T/P \tag{A.27}$$

$$(h_{\tau})_{\alpha} = \mathcal{R}\left[\frac{7+3\alpha}{2} + (1-\alpha)\frac{d\mathcal{E}}{d\tau}\right] \tag{A.28}$$

$$(h_{\alpha})_{T} = RT \left(\frac{3}{2} + \frac{Q_{D} - \Sigma}{T} \right) \tag{A.29}$$

Substituting these in Eq. (A. 23) and simplifying,

$$\frac{h_p + h_u \propto e_p}{h_p} = \frac{7 + 3\alpha + 2(1 - \alpha)\frac{d\xi}{d\tau} + \alpha e(1 - \alpha e^2)(\frac{3}{2} + \frac{\theta_p - \xi}{\tau})^2}{\alpha e(1 - \alpha e)\left[\frac{7 + 3\alpha}{2} + (1 - \alpha)\frac{d\xi}{d\tau}\right]\left[\frac{2}{\alpha(1 - \alpha)} + \frac{3}{2} + \frac{\theta_p - \xi}{\tau}\right]} (A.30)$$

$$K = \Psi L_{\alpha} \frac{(h\rho + h_{\alpha} \alpha e \rho)}{h\rho} = -k_{d} \frac{\rho}{m_{\alpha} \alpha} \left[1 + \frac{\alpha_{e} (1 - \alpha_{e}^{2})(\frac{3}{2} + \frac{\theta_{p} - \xi}{2})^{2}}{7 + 3\alpha + 2(1 - \alpha)\frac{d\xi}{dT}} \right]$$
(A. 31)

The frozen sound speed is

$$\mathcal{A}_{s}^{2} = -\frac{(h_{p})_{P,\alpha}}{(h_{p})_{P,\alpha} - 1/p}$$

$$= -\frac{(h_{T})_{\alpha}(T_{p})_{P,\alpha}}{(h_{T})_{\alpha}(T_{p})_{P,\alpha}} - \frac{1/p}{p}$$

$$= -\frac{(-RT)_{\alpha}(T_{p})_{P,\alpha}}{\frac{1}{2} + (1-\alpha)\frac{d\xi}{dT}}$$

$$= -\frac{(-RT)_{\alpha}(T_{p})_{P,\alpha}}{\frac{1}{2} + (1-\alpha)\frac{d\xi}{dT}} - \frac{1/p}{p}$$

$$= \frac{(-RT)_{\alpha}(T_{p})_{P,\alpha}}{\frac{1}{2} + (1-\alpha)\frac{d\xi}{dT}} - \frac{1/p}{p}$$

$$= \frac{(-RT)_{\alpha}(T_{p})_{P,\alpha}}{\frac{$$

where

$$A' = \frac{1}{1+\alpha} \left[(5+\alpha) + 2(1-\alpha) \frac{d\varepsilon}{d\tau} \right]$$

$$\Gamma_{\downarrow} = \frac{A'+2}{A'}$$
(A. 33)

The equilibrium sound speed is

$$Q_{e}^{z} = -\frac{(h_{\rho})_{p,\alpha} + (h_{\alpha})_{p,\rho} (\alpha_{e\rho})_{p}}{(h_{\rho})_{p,\alpha} + (h_{\alpha})_{p,\rho} (\alpha_{e\rho})_{p} - \frac{1}{\rho}}$$

$$\tag{18}$$

$$=-\frac{(h_{\tau})_{\alpha}(T_{\rho})_{p,\alpha}+\left[(h_{\tau})_{\alpha}(T_{\alpha})_{p,\beta}+(h_{\alpha})_{\tau}\right]\frac{(\alpha_{ep})_{\tau}+(\alpha_{ep})_{p,\alpha}}{1-(\alpha_{ep})_{\rho}(T_{\alpha})_{p,\alpha}}}{(h_{\tau})_{\alpha}(T_{\rho})_{p,\alpha}+\left[(h_{\tau})_{\alpha}(T_{\alpha})_{p,\beta}+(h_{\alpha})_{\tau}\right]\frac{(\alpha_{ep})_{\rho}(T_{\alpha})_{p,\alpha}}{1-(\alpha_{ep})_{\rho}(T_{\alpha e})_{p,\rho}}-\frac{1}{9}}$$

$$=\frac{(h_{\tau})_{\alpha}[T_{\rho})_{\rho,\alpha}+(T_{\alpha})_{\rho,\rho}(\alpha_{\rho})_{\tau}]+(h_{\alpha})_{\tau}[(\alpha_{\rho})_{\tau}+(\alpha_{\rho})_{\tau}]_{\rho,\alpha}}{\frac{1}{\rho}-(h_{\tau})_{\alpha}(T_{\rho})_{\rho,\alpha}-(\alpha_{\rho})_{\rho}[\frac{1}{\rho}(T_{\alpha})_{\rho,\rho}+(h_{\alpha})_{\tau}(T_{\rho})_{\rho,\alpha}]}$$

Substituting for the various quantities and simplifying

$$Q_{e}^{2} = \frac{7+3\alpha+2(1-\alpha)\frac{d\xi}{d\tau}+\alpha(1-\alpha^{2})(\frac{3}{2}+\frac{\theta_{0}-\xi}{\tau})^{2}}{(2-\alpha)\left(\frac{5+\alpha}{2}+(1-\alpha)\frac{d\xi}{d\tau}\right)+\alpha(1-\alpha)\left(\frac{1}{2}+\frac{\theta_{0}-\xi}{\tau}\right)^{2}}$$

$$=\frac{A'+R+\alpha(1-\alpha)\left(\frac{3}{2}+\frac{\theta_{0}-\xi}{\tau}\right)^{2}}{(2-\alpha)\left(\frac{1+\alpha}{2}\right)A'+\alpha(1-\alpha)\left(\frac{1}{2}+\frac{\theta_{0}-\xi}{\tau}\right)^{2}}(1+\alpha)RT$$

$$=\frac{A'+2+\alpha(1-\alpha)\left(\frac{3}{2}+\frac{\theta_{0}-\xi}{\tau}\right)^{2}}{B_{f}'}(1+\alpha)RT$$

$$=\Gamma_{e}(1+\alpha)RT \qquad (A.34)$$

where

$$B_{t}' = \frac{2-\alpha}{2} \left(5+\alpha+2\left(1-\alpha\right) \frac{d\varepsilon}{d\tau} \right) + \alpha \left(1-\alpha\right) \left(\frac{1}{2} + \frac{\beta_{0}-\varepsilon}{\tau} \right)^{2}$$

$$= \frac{2-\alpha}{2} \left(1+\alpha \right) A' + \alpha \left(1-\alpha \right) \left(\frac{1}{2} + \frac{\beta_{0}-\varepsilon}{\tau} \right)^{2} \qquad (A.35)$$

$$\Gamma_{e} = \frac{A'+2+\alpha \left(1-\alpha\right) \left(\frac{3}{2} + \frac{\beta_{0}-\varepsilon}{\tau} \right)^{2}}{B_{t}'}$$

$$\beta = \frac{K_*}{a_f^*} = -\frac{1}{a_f^*} \frac{R_a^* \rho^*}{m_a \alpha^*} \left[1 + \frac{\alpha^* (1 - \alpha^*) (\frac{3}{2} + \frac{Q_b - \xi^*}{T^*})^2}{(A'^* + 2)} \right]$$
 (A. 36)

Estimation of the errors in the approximate Eqs. (31) and (37).

In deriving the relations between sound speeds and flow speeds in section 2.d,

$$a_t^2 \approx \frac{A^* + 1}{A^*} a_t^{*2} - \frac{q^2}{A^*}$$
 (31)

$$a_e^2 \approx \frac{a_f^{*2} - q^2}{B_f^*} - a_e^{*2}$$
 (37)

A and B_f in the denominators were replaced by A* and B* . The errors involved in these approximations are evaluated here.

$$A(\alpha, T) = \frac{1}{1+\alpha} \left[5 + \alpha + 2(1-\alpha) \frac{d\xi}{d\tau} \right] \left[7 + 3\alpha + 2(1-\alpha) \frac{\xi}{\tau} + 2\alpha \frac{\varphi}{\tau} \right] / \left[7 + 3\alpha + 2(1-\alpha) \frac{\xi}{\tau} \right]$$

$$= \frac{A'}{(A'+2)(1+\alpha)} \frac{2A}{RT}$$
(A. 37)

where

$$\mathcal{E} = \frac{\theta_{v}}{e^{\theta v/T} - 1}$$

and

$$\xi_{\mathsf{T}} = \frac{d\,\xi}{d\,\mathsf{T}} = \left(\frac{\varrho_{\mathsf{V}}}{\mathsf{T}(e^{\varrho_{\mathsf{V}}/\mathsf{T}} - \mathsf{J})}\right)^{2} e^{\varrho_{\mathsf{V}}/\mathsf{T}} = \left(\frac{\xi}{\mathsf{T}}\right)^{2} e^{\varrho_{\mathsf{V}}/\mathsf{T}}$$

Expanding A (α , τ) in Taylor's series about α^*, τ^* , and keeping only first order terms: -

$$A(\alpha, T) = A(\alpha^*, T^*) + \left(\frac{\partial A}{\partial \alpha}\right)^* \alpha' + \left(\frac{\partial A}{\partial T}\right)^* T' \qquad (A.38)$$

From Eq. (A.37)

$$\log A = \log A' + \log \frac{2A}{RT} - \log(A'+2) - \log(1+\alpha)$$

$$\frac{1}{A} \stackrel{\partial A}{\partial \alpha} = \frac{1}{A'} \stackrel{\partial A'}{\partial \alpha} + \frac{1}{A} \stackrel{\partial A}{\partial \alpha} - \frac{1}{A'+2} \stackrel{\partial A'}{\partial \alpha} - \frac{1}{1+\alpha}$$

$$\frac{\partial A'}{\partial \alpha} = -\frac{1}{1+\alpha} - \frac{5+\alpha}{(1+\alpha)^2} + 2 \frac{d\varepsilon}{dT} \left[-\frac{1}{1+\alpha} - \frac{1-\alpha}{(1+\alpha)^2} \right]$$

$$= -\frac{A}{(1+\alpha)^2} \left(1 + \frac{d\varepsilon}{dT} \right)$$

$$\varepsilon_T = \frac{d\varepsilon}{dT} = \left(\frac{\varepsilon}{T} \right)^2 e^{\frac{G_0}{T}}$$

$$\left(\stackrel{\partial A}{\partial \alpha} \right)^* = A^* \left[-\frac{1}{1+\alpha} + \frac{8(1+\varepsilon_{T*})}{A'^*(A'^*+2)(1+\alpha^*)^2} + \frac{A_{\alpha^*}}{A^*} \right] \qquad (A.39)$$

$$\frac{1}{A} \stackrel{\partial A}{\partial T} = \frac{1}{A'} \stackrel{\partial A'}{\partial T} + \frac{1}{A} \stackrel{\partial A}{\partial T} - \frac{1}{T} - \frac{1}{A'+2} \stackrel{\partial A'}{\partial T}$$

$$\frac{\partial A'}{\partial T} = \frac{2(1-\alpha)}{1+\alpha} \frac{d^2\varepsilon}{dT^2}$$

$$\left(\stackrel{\partial A}{\partial T} \right)^* = A^* \left[-\frac{1}{T^*} + \frac{4(1-\alpha^*)}{(1+\alpha^*)A'^*(A'^*+2)} \varepsilon_{TT}^* + \frac{A_T^*}{2^*} \right] \qquad (A.40)$$

$$(A(\alpha, T) = A^* \left[1 - \frac{\alpha'}{H \alpha''} \left[1 + \frac{8(1 + \xi_T^*)}{A'''(A'' + 2)(1 + \alpha'')} - \frac{h_{\alpha''}^*}{\lambda''} \right] + \frac{T'}{T''} \left[-1 + \frac{T^* h_T^*}{h^*} + \frac{4(1 - \lambda)T^* \xi_{TT}^*}{A''' (A'' + 2)(1 + \alpha'')} \right]$$

where

$$T^* \mathcal{E}_{T^*T^*} = T^* \left(\frac{d^2 \mathcal{E}}{dT^2} \right)^* = \left(\frac{\mathcal{E}^*}{T^*} \right)^2 e^{0\nu f^*} \left(e^{0\nu f^*} + 1 \right) - 2 \right] \tag{A.41}$$

$$B_{f}(\lambda,T) = \frac{(2-\alpha)\left(5+\alpha+2(1-\alpha)\frac{d\xi}{dT}\right) + \alpha(1-\alpha)\left(\frac{1}{2} + \frac{O_{D}-\xi}{T}\right)^{2}}{7+3\alpha+2(1-\alpha)\xi_{T} + \alpha(1-\alpha^{2})\left(\frac{3}{2} + \frac{O_{D}-\xi}{T}\right)^{2}} \left(\frac{1+3\alpha}{2}T + (1-\alpha)\xi_{T} + \lambda G_{T}^{2}(A.42)\right)$$

$$= \frac{C}{D} \cdot \frac{A}{R}$$

$$\log B_{f} = \log C - \log D + \log A/R$$

$$\frac{1}{B_{f}} \frac{\partial B_{f}}{\partial \alpha} = \frac{1}{C} \frac{\partial C}{\partial \alpha} - \frac{1}{D} \frac{\partial D}{\partial \alpha} + \frac{1}{A} \frac{\partial A}{\partial \alpha}$$

$$\frac{\partial C}{\partial \alpha} = -3 - 2\alpha + 2\xi_{T}(-3 + 2\alpha) + (1-2\alpha)\left(\frac{1}{2} + \frac{O_{D}-\xi}{T}\right)^{2}$$

$$\frac{\partial D}{\partial \alpha} = 3 - 2\xi_{T} + (1-3\alpha^{2})\left(\frac{3}{2} + \frac{O_{D}-\xi}{T}\right)^{2} \qquad (A.43)$$

$$\frac{1}{B_{f}} \frac{\partial B_{f}}{\partial T} = \frac{1}{C} \frac{\partial C}{\partial \alpha} - \frac{1}{D} \frac{\partial D}{\partial T} + \frac{1}{A} \frac{\partial A}{\partial T}$$

$$\frac{\partial C}{\partial T} = 2\left(1-\alpha\right)\left(2-\alpha\right)\xi_{TT} + 2\alpha\left(1-\alpha\right)\left(\frac{3}{2} + \frac{O_{D}-\xi}{T}\right)\left(\frac{\xi-O_{F}}{T^{2}} - \frac{\xi_{T}}{T}\right)$$

$$\frac{\partial D}{\partial T} = R\left(1-\alpha\right)\xi_{TT} + 2\alpha\left(1-\alpha^{2}\right)\left(\frac{3}{2} + \frac{O_{D}-\xi}{T}\right)\left(\frac{\xi-O_{F}}{T^{2}} - \frac{\xi_{T}}{T}\right) \qquad (A.44)$$

Expanding B_{f} (\checkmark , \top) in Taylor's series and keeping up to first order terms,

$$B_{f}(\lambda, T) = B_{f}(\lambda^{*}, T^{*}) + \lambda' \left(\frac{\partial B_{f}}{\partial \lambda}\right)^{*} + T' \left(\frac{\partial B_{f}}{\partial T}\right)^{*}$$
(A. 45)

Substituting for $\frac{\partial B_i}{\partial a}$ and $\frac{\partial B_i}{\partial T}$

$$B_{\zeta}(\alpha, T) = B_{\zeta}^{*} \left\{ 1 + \alpha' \left[\frac{1}{c'} \left(\frac{\partial \zeta}{\partial \alpha} \right)_{*} - \frac{1}{D} \left(\frac{\partial D}{\partial \alpha} \right)_{*} + \frac{h_{\zeta}^{*}}{h^{*}} \right] + T' \left[\frac{1}{c'} \left(\frac{\partial C}{\partial \gamma} \right)_{*} - \frac{1}{D^{*}} \left(\frac{\partial D}{\partial \gamma} \right)_{*} + \frac{h_{\zeta}^{*}}{h^{*}} \right] \right\} \quad (A. 46)$$

It can be shown that for $0 \ge \theta_0/T \ge 0$ $0 \le \varepsilon/T \le 1$ $0 \le \varepsilon_T \le 1$ (A. 47)

and $TE_{TT} \approx 0$

Considering only cases where Θ_b/\mathcal{T} is equal to or less than one, E/\mathcal{T} and $E_{\mathcal{T}}$ may be replaced by unity for the error estimation.

Thus it can be shown that

$$A' = \frac{5+\alpha+2(1-\alpha)}{(1+\alpha)} \simeq \frac{7-\alpha}{1+\alpha}$$
 (A. 48)

is always greater than 3 which value it attains when α = 1, and always less than 7 which value it attains when α = 0. From this

$$63 \ge A'(A'+2)(1+\alpha) \ge 30 \text{ for } 0 \le \alpha \le 1$$
 (A. 49)

Thus the 2nd term in the coefficient $\alpha'/1+\alpha*$ in Eq. (A. 41) is always less than 0.54. The 3rd term in the coefficient of T'/T* in Eq. (A. 41) is very nearly zero.

Therefore
$$(h \propto /h) = \frac{3/2T + \theta_D - \varepsilon}{\frac{7+3 \propto}{2} T + (I-\propto) \varepsilon + \propto \theta_D} \simeq \frac{0.5 + \theta_D/T}{4.5 + \propto (0.5 + \theta_D/T)}$$
(A. 50)

or
$$(1-h_{\alpha}/h) \approx \frac{4+0.5\alpha-(1-\alpha)\theta_{D}/T}{4.5+0.5\alpha+\alpha\theta_{D}/T} < 1$$

Also,

$$-1 + \frac{Th_{T}}{h} = \frac{-\left[\frac{7+3\alpha}{2} + (1-\alpha)\mathcal{E}/_{7} + \alpha\theta_{D}/_{T}\right] + \left[\frac{7+3\alpha}{2} + (1-\alpha)\mathcal{E}_{T}\right]}{\frac{7+3\alpha}{2} + (1-\alpha)\mathcal{E}/_{T} + \alpha\theta_{D}/_{T}} \approx \frac{\alpha\theta_{D}/_{T}}{4\cdot5+\cdot5\alpha+\alpha\theta_{D}/_{T}}$$

since the denominator is always larger than the numerator. From Eqs. (A. 49) to (A. 51), one can show that the coefficients of $\alpha'/1+\alpha^*$ and T'/T^* in Eq. (A. 41) for A, are always less than 1. i.e.

$$-1 + \frac{T^* h_{T^*}}{h^*} + \frac{4(1-\alpha^*)T^* \mathcal{E}_{TT}^*}{A'^* (A'^* + 2)(1+\alpha^*)} < 1$$

In a similar way, it can be shown that the coefficients of α' and τ' in Eq. (A. 46) for B₁ are also less than unity. Thus replacing A by A* and B₂ by B₃* in deriving Eqs. (31) and (37) in the test will not lead to large errors.

Alternative Derivation of Eq. (19):-

In deriving Eq. (19), it was assumed that the dissociation is only slightly out of equilibrium. This restriction can be removed as follows:-

Consider the Taylor's series of the quantity ψ .L in Eq. (1) about the reference state values. Then

$$\Psi (p, \rho, \alpha) \vdash (p, \rho, \alpha) = (\Psi \vdash)^* + (\Psi \vdash)_{p*} p' + (\Psi \vdash)_{\rho*} \varrho' + (\Psi \vdash)_{\alpha*} \alpha'$$
(A. 52)

analogous to Eq. (3). Then

$$\frac{D_{t}(D_{x})}{D_{t}(D_{t})} = \frac{D_{t}(\Psi L)}{D_{t}} = (\Psi L)_{p*} \frac{D_{t}^{p'}}{D_{t}^{p'}} + (\Psi L)_{p*} \frac{D_{t}^{p'}}{D_{t}^{p'}} + (\Psi L)_{q*} \frac{D_{q'}}{D_{t}^{p'}}$$
(A. 53)

From the energy equation, Eq. (10) and Eq. (13),

$$\frac{D\alpha}{Dt} = \frac{D\alpha'}{Dt} = -\frac{(h_p - 1/\rho)}{h_\alpha} \frac{D\rho}{Dt} - \frac{h_\rho}{h_\alpha} \frac{D\rho}{Dt}$$
(A. 54)

which upon substitution in Eq. (A.53) gives

$$\frac{D_{t}(D_{t}^{\alpha})}{D_{t}} = \left[(\Psi L)_{p*} - (\Psi L)_{x*} \frac{h_{p} - V\rho}{h_{w}} \right] \frac{D\rho}{Dt} + \left[(\Psi L)_{p*} - (\Psi L)_{x*} \frac{h_{p}}{h_{w}} \right] \frac{D\rho}{Dt}$$

$$= (\Psi L)_{\alpha*} \left\{ \left[\frac{(\Psi L)_{p*}}{(\Psi L)_{\alpha*}} - \left(\frac{h_{p} - V\rho}{h_{w}} \right) \right] \frac{D\rho}{Dt} + \left[\frac{(\Psi L)_{p*}}{(\Psi L)_{\alpha*}} - \frac{h_{p}}{h_{w}} \right] \frac{D\rho}{Dt} \right\} (A.55)$$

Now define α_e , the local equilibrium value of α , as that given by

$$L(p, e, \alpha_e) = 0 \tag{A.56}$$

Then

$$\Psi(p, \rho, \alpha_e) \perp (p, \rho, \alpha_e) = 0 \tag{A.57}$$

as long as ψ is finite. The total differential of Eq. (A. 57) gives

$$(\Psi L)_{p} dp + (\Psi L)_{p} d\theta + (\Psi L)_{q} d\alpha_{e} = 0$$
 (A.58)

From Eq. (A.58), one obtains

$$\alpha_{ep} = -\frac{(\psi_L)_p}{(\psi_L)_{el}} \tag{A.59}$$

$$\alpha_{ee} = -\frac{(\Upsilon L)_e}{(\Upsilon L)_{\alpha}} \tag{A.60}$$

which upon substitution in Eq. (A. 55) gives

$$\frac{D}{Dt} \left(\frac{D\alpha}{Dt} \right) = (\Psi L)_{\alpha^{*}} \left\{ \left[-\alpha_{ep} - \frac{h_{e} - V_{e}}{h_{\alpha}} \right] \frac{Dp}{Dt} + \left[-\alpha_{ep} - \frac{h_{e}}{h_{\alpha}} \right] \frac{Dp}{Dt} \right\}$$

$$= -(\Psi L)_{\alpha^{*}} \left(\frac{h_{e} + h_{\alpha} \alpha_{ee}}{h_{\alpha}} \right) \left\{ \frac{h_{p} + h_{\alpha} \alpha_{ep} - V_{e}}{h_{p} + h_{\alpha} \alpha_{ep}} \frac{Dp}{Dt} + \frac{Dp}{Dt} \right\}$$

$$= -(\Psi L)_{\alpha^{*}} \left(\frac{h_{e} + h_{\alpha} \alpha_{ep}}{h_{\alpha}} \right) \left\{ \frac{1}{\alpha_{e}^{2}} e^{\overrightarrow{q}} \cdot \frac{D\overrightarrow{q}}{Dt} - e \operatorname{div} \cdot \overrightarrow{q} \right\}$$

$$= -(\Psi L)_{\alpha^{*}} \frac{e(h_{p} + h_{\alpha} \alpha_{ee})}{h_{\alpha}} \left[\frac{1}{\alpha_{e}^{2}} e^{\overrightarrow{q}} \cdot \frac{D\overrightarrow{q}}{Dt} - \operatorname{div} \cdot \overrightarrow{q} \right]$$

$$= \Psi^{*} L_{\alpha^{*}} \left(1 + \frac{\Psi_{\alpha^{*}} L}{\Psi^{*} L_{\alpha^{*}}} \right) \frac{e(h_{e} + h_{\alpha} \alpha_{ee})}{h_{\alpha}} \left[\operatorname{div} \cdot \overrightarrow{q} - \frac{1}{\alpha_{e}^{2}} e^{\overrightarrow{q}} \cdot \frac{D\overrightarrow{q}}{Dt} \right] \tag{A.61}$$

by the use of Eq. (8), (9) and the definition of a^2 given in Eq. (18). It may be noted that Eq. (A. 61) differs from Eq. (17) in the text by the factor $(1 + \frac{2}{4})^2 + \frac{1}{4}$

Finally eliminating $D\alpha/Dt$ on the LHS of Eq. (A. 61) by the use of Eq. (16), one obtains,

$$\frac{D}{Dt} \left\{ \frac{\rho h_e}{h_u} \left[\text{div.} \vec{q} - \frac{1}{\alpha_e^2} \frac{D \vec{q}^2/2}{Dt} \right] \right\} = (\Psi L)_{uv} \frac{\rho (h_e + h_u \alpha_{ee})}{h_u} \left[\text{div.} \vec{q} - \frac{1}{\alpha_e^2} \vec{q} \cdot \frac{D\vec{q}}{Dt} \right] (A. 62)$$

in the place of Eq. (19) in the text.

Vibrational and Dissociational Nonequilibrium:-

In any real flow, the vibration as well as dissociation will be out of equilibrium and one would have to deal with fully frozen characteristics for the calculation of the supersonic flow region by the method of characteristics. The analysis of the flow in the fully frozen sonic region is much more complex

than the one considered in the text which is for the partially frozen sonic region. However a general idea of what one might expect from the results of the partially frozen flow may be obtained as follows:

In this case either the vibrational energy $\boldsymbol{\xi}_v$ or vibrational temperature T_v is to be taken as an additional variable. Thus

$$h = h(T, \alpha, \varepsilon_{\nu}) = h(p, \rho, \alpha, \varepsilon_{\nu}) \tag{A.63}$$

$$\frac{Dh}{Dt} = (h_p)_{e,\alpha,\epsilon_v} \frac{Dp}{Dt} + (h_e)_{p,\alpha,\epsilon_v} \frac{De}{Dt} + (h_\alpha)_{p,e,\epsilon_v} \frac{D\alpha}{Dt} + (h_{\epsilon_v})_{p,e,\alpha} \frac{D\epsilon_v}{Dt}$$
(A. 64)

which on substitution in the energy equation, Eq. (10), gives

$$(h_{p}-V_{p})\frac{D_{t}^{p}}{D_{t}^{t}}+h_{t}\frac{D_{t}^{q}}{D_{t}^{t}}+h_{u}\frac{D_{x}^{q}}{D_{t}^{t}}+h_{\varepsilon_{v}}\frac{D_{\varepsilon_{v}^{q}}}{D_{t}^{t}}=0$$
(A. 65)

where, h_p , h_{ℓ} , h_{α} in Eq. (A.65) are different from those in Eq. (13) in the text which contain also the contributions from $h_{\ell \nu}$ $\frac{D \ell \nu}{D \ell}$ where, $\ell \nu$ is a function of T alone, i.e. $T \equiv T'_v$.

For uncoupled vibrational and dissociational nonequilibrium, Eq. (A.53) for D/Dt (D α /Dt) is still valid and ϵ_{ν} satisfies the London-Teller equation, namely,

$$\frac{D\mathcal{E}_{v}}{Dt} = \frac{\mathcal{E}_{w} - \mathcal{E}_{v}}{\mathcal{T}_{v}}$$
 (A. 66)

where, T_v is the vibrational relaxation time and E_v is E_v evaluated by replacing T_v by T. Let T_v differ from T by a small amount, then

$$T_{\nu} = T + T'$$

$$\varepsilon_{\nu} = \varepsilon_{\infty} + \varepsilon'$$
(A. 67)

Also

$$h_{\epsilon_v} = h_{\epsilon_w} = (1 - \alpha)$$

$$h_{\varepsilon_{v}} \frac{D\varepsilon_{v}}{Dt} = h_{\varepsilon_{w}} \frac{D\varepsilon_{w}}{Dt} + h_{\varepsilon_{w}} \frac{D\varepsilon'}{Dt}$$

$$= h_{\varepsilon_{w}} \varepsilon_{w\tau} \left(T_{p} \frac{Dp}{Dt} + T_{p} \frac{Dp}{Dt} + T_{u} \frac{Du}{Dt} \right) + h_{\varepsilon_{w}} \frac{D\varepsilon'}{Dt}$$
(A. 68)

where the subscripts denote differentiation. Substituting Eq. (A. 68) in Eq. (A. 65) and rearranging one may write

$$\left(h_{u}+h_{\varepsilon_{\bullet}}\varepsilon_{\bullet\tau}T_{u}\right)\frac{D\alpha}{Dt}=-\left(h_{\rho}+h_{\varepsilon_{\bullet}}\varepsilon_{\bullet\tau}T_{\rho}-\frac{1}{\rho}\right)-\left(h_{\rho}+h_{\varepsilon}\varepsilon_{\bullet\tau}T_{\rho}\right)\frac{D\rho}{Dt}-h_{\varepsilon_{\bullet}}\frac{D\varepsilon'}{Dt} \qquad (A. 69)$$

Substituting Eq. (A. 69) for $D\alpha'/DT = D\alpha/Dt$ on the RHS in Eq. (A. 53) and making use of relations (A. 59), (A. 60), one has

$$\frac{D}{Dt}\left(\frac{D\alpha}{Dt}\right) = (\Psi L)_{\alpha w} \left\{ -\left[\alpha_{ep} + \frac{h_{p} + h_{ew} \mathcal{E}_{\omega T} T_{p} - 1/\rho}{h_{\alpha} + h_{ew} \mathcal{E}_{\omega T} T_{\alpha}}\right] \frac{DP}{Dt} - \left[\alpha_{ep} + \frac{h_{p} + h_{ew} \mathcal{E}_{\omega T} T_{\alpha}}{h_{\alpha} + h_{ew} \mathcal{E}_{\omega T} T_{\alpha}}\right] \frac{DP}{Dt} - \left(\frac{h_{ew}}{h_{\alpha} + h_{ew} \mathcal{E}_{\omega T} T_{\alpha}}\right) \frac{DE'}{Dt} \right\}$$

$$= (\Psi L)_{\alpha w} \left[\alpha_{ep} + \frac{h_{e} + h_{ew} \mathcal{E}_{\omega T}}{h_{\alpha} + h_{ew} \mathcal{E}_{\omega T}} \frac{1}{T_{\alpha}} \frac{DP}{a^{2}} - \frac{DP}{Dt} - \frac{DP}{h_{e} + h_{\alpha} \alpha_{ep} + h_{e} \mathcal{E}_{\omega T}} \frac{DE'/Dt}{(T_{e} + T_{\alpha} \alpha_{ep})} \right]$$

$$\approx (\Psi L)_{\alpha w} \left[\alpha_{ep} + \frac{h_{e} + h_{ew} \mathcal{E}_{\omega T}}{h_{\alpha} + h_{ew} \mathcal{E}_{\omega T}} \frac{1}{T_{\alpha}} \left(\frac{1}{\alpha_{e}^{2}} \frac{DP}{Dt} - \frac{DP}{Dt} \right) \right] (A.70)$$

Since the coefficient of DE'/Dt can be shown to be smaller than unity and a_e is the equilibrium speed of sound given by

$$\alpha_e^2 = -\frac{h_e + h_u \alpha_{ee} + h_{ew} \mathcal{E}_{\omega T} (T_p + T_u \alpha_{ee})}{h_p + h_u \alpha_{ep} + h_{ew} \mathcal{E}_{\omega T} (T_p + T_u \alpha_{ep}) - \sqrt{\rho}}$$
(A.71)

Using Eq. (A.65), the RHS of Eq. (A.70) may be written as

$$\frac{D}{Dt} \left(\frac{D\alpha}{Dt} \right) = -\frac{D}{Dt} \left\{ \frac{h_e}{h_a} \left[\frac{(h_e - 1/e)}{h_e} \frac{DP}{Dt} + \frac{DP}{Dt} + \frac{h_{\epsilon \nu}}{h_e} \frac{DEv}{Dt} \right] \right\}$$

$$\approx \frac{D}{Dt} \left\{ \frac{h_e}{h_a} \left[\frac{1}{\alpha_s^2} \frac{DP}{Dt} - \frac{DP}{Dt} \right] \right\} \tag{A.72}$$

where the fully frozen speed of sound $\mathbf{a}_{\mathbf{f}}$ is given by

$$\alpha_f^2 = -\frac{(h_e)_{p,\alpha,\epsilon_v}}{(h_p)_{e,\alpha,\epsilon_v} - 1/\varrho} \tag{A.73}$$

and the $DE\sqrt{Dt}$ term was neglected since it can be shown that its coefficient $h_{E\sqrt{h_e}}$ is smaller than unity. Equations (A. 70), (A. 72) together give, by use of Eqs. (8) and (9)

$$\frac{D}{Dt} \left\{ \frac{\rho h_e}{h_u} \left(\text{div.} \vec{q} - \frac{1}{Q_e^2} \vec{q} \cdot \frac{D\vec{q}}{Dt} \right) \right\} \approx \left(\Psi L \right)_{x} \rho \left[\alpha_{e\rho} + \frac{h_e + h_{e\omega} \mathcal{E}_{\omega\tau} T_e}{h_u + h_{e\omega} \mathcal{E}_{\omega\tau} T_u} \right] \left(\text{div.} \vec{q} - \frac{1}{Q_e^2} \vec{q} \cdot \frac{D\vec{q}}{Dt} \right) \quad (A.74)$$

One may note that the expression for a_f^2 given in Eq. (A.73) explicitly excludes all vibrational energy contributions and thus it is the fully frozen speed of sound while the equilibrium speed of sound given by Eq. (A.71) is the same as before since it includes the vibrational energy contributions.

Since Eq. (A. 74) differs little from Eq. (A. 62) except in the definition of a_f , one can accept the vibrational-dissociational nonequilibrium results to be very similar to that of vibrational equilibrium-dissociational nonequilibrium results.

APPENDIX B

TRANSONIC FLOW IN A NOZZLE FOR PERFECT GASES

The flow field in the sonic region of a deLaval nozzle for perfect gas flows is described in this Appendix as a ready reference for comparison with the reacting gas flows described in the text. All of these results are taken from Ref. 10.

Let q, a, A, θ be the flow speed, sound speed, specific enthalpy and streamline angle respectively. It has been shown in Ref. 10 that a perturbation velocity potential Ψ can be introduced such that

$$\begin{aligned}
q_{x} &= a^{*}(i + \mathcal{Q}_{x}) \\
q_{y} &= a^{*}\mathcal{Q}_{y}
\end{aligned} (B. 1)$$

where a* is the critical speed (i.e. where f = a) and f_x , φ_x and f_y , φ_y are the x and y components of the velocity and perturbation respectively and φ satisfies the equation

$$-(8+1)\varphi_{x} + 4\psi_{yy} = 0$$
 (B. 2)

The solution of this equation valid in the sonic region of a de Laval nozzle is shown to be

$$\varphi = (\frac{x^2}{2} + (y+1)c^2\frac{xy^2}{2} + (y+1)^2c^3\frac{y^4}{24}$$
 (B.3)

where C is a positive constant and γ is the ratio of specific heats. The x and y components of the perturbation velocity are then,

$$\Psi_{x} = C\chi + (\gamma + 1) \frac{c^{2}\psi^{2}}{2}$$
(B. 4)

$$4y = (y+1)c^{2}y\left[x+\frac{(y+1)cy^{2}}{4}\right]$$
 (B.5)

from which the sonic line is given approximately by putting $\forall_x = 0$ as

$$O = \chi + (\gamma + 1) C \gamma / 6 \tag{B.6}$$

and the line of horizontal velocity or the locus of points where the velocity vector is parallel to the nozzle axis is given by putting $\psi_{\mu} = 0$ as

$$0 = \chi + \frac{(\lambda + i)cy^2}{6}$$
 (B.7)

From the approximation $q \approx a^+ + \psi_{\kappa}$, it will be seen from Eqs. (B. 4), (B. 6), and (B. 7) that the constant velocity curves, sonic line and line of horizontal velocity are all parabolas.

It is also shown that the characteristic directions are approximately given by

$$\frac{dy}{dx} = (3+1)^{-1/2} \left(\frac{g'}{a^2}\right)^{-1/2}$$
 (B.8)

along which q and θ are related as

$$\sqrt{y+1} = \frac{2}{3} \left(\frac{q'}{a''} \right)^{\frac{1}{2}} = \theta = \text{constant}$$
 (B. 9)

where q' is the deviation of the velocity from the critical speed . i.e. $q'=q-\alpha * d\psi_{x}$

From Eqs. (B.4) and B.8), two special curves which are characteristics are shown to exist and are given by

$$\frac{\mathcal{Z}}{\mathcal{Y}} = -c \frac{\mathcal{Y} + 1}{2} \tag{B. 10}$$

$$\frac{\chi}{V} = c \frac{V+1}{4} \tag{B.11}$$

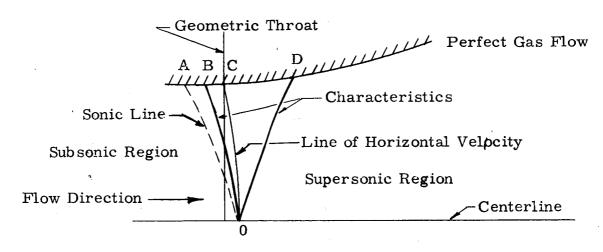
The first curve (see line OB in Sk. 4) is known as the limiting characteristic since it divides the flow into two distinct regions:

I) that in the subsonic part of the nozzle and that in the supersonic part of the nozzle (AB) which influences the subsonic flow II) the remaining supersonic flow beyond B.

It is also shown that the sonic line and the limiting characteristic meet the nozzle wall upstream of the geometric throat C and that the sonic line and line of horizontal velocity meet on the axis as shown in Sk. 4. Any changes in the nozzle contour downstream of point B will not influence the flow in the region

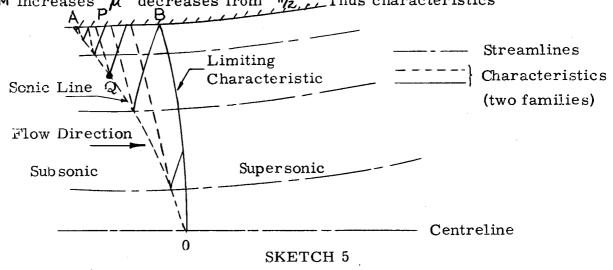
upstream of the characteristic passing

and



SKETCH 4

through B, whereas changes in the nozzle contour between B and A will influence the sonic line and thus affect the entire flow including the subsonic region. To give an insight into the characteristic network in the region between the sonic line and the limiting characteristic, an exaggerated sketch of this region is shown below. The characteristics are inclined to the streamlines at the Mach angle $\frac{1}{L}\mu$ where $\mu = \frac{1}{L}\mu$. For $M = \frac{1}{L}\mu$, $\mu = \frac{\pi}{L}\mu$ and as M increases μ decreases from μ characteristics



at a point Q on the sonic line are perpendicular to the streamline passing through it whereas at a point P on the nozzle wall, which is also a streamline, they are inclined at an angle slightly less than $\pi/2$, and along each one of these characteristics the changes in q and θ are related by Eq. (B. 9)

Comparison of Reacting and Perfect Gas Flows

For a perfect gas, the specific enthalpy A and the sound speed are related as

$$\mathcal{L} = \frac{a^2}{\gamma - 1} \tag{B. 12}$$

Comparing Eq. (B.12) with Eqs. (26) and (33) in the text, one may note that

$$y_{\overline{f}}^{\prime} - 1 = \frac{2}{A}$$
 (B. 13)

$$y_e - 1 = \frac{2}{B_f}$$
 (B. 14)

Eqs. (B. 13) and (B. 14) may be taken as the definition of γ_{3} and γ_{4} . They may be considered as fictitious isentropic indices for partially frozen and equilibrium cases in reacting gas flows. The true expressions for these quantities in the present cases are given by Eqs. (A. 32) and (A. 34). From Eqs. (B. 13) and (B. 14), the parameters P and N given by Eq. (48) in the text will be

$$P = 2 \frac{A^{+}+1}{A^{+}} = (2 + \frac{1}{2} - 1) = \frac{1}{2} + 1$$
(B. 15)

$$N = \frac{2 q_{t}^{**}}{a_{e}^{**2}} \left(1 + \frac{a_{t}^{**2}}{B_{t}^{**} d_{e}^{**2}} \right) = \frac{a_{t}^{**2}}{a_{e}^{**2}} \left[2 + \frac{a_{t}^{**2}}{a_{e}^{**2}} (\beta_{e}^{**-1}) \right] \quad (B. 16)$$

In the limit of equilibrium flow, (see Sec. 3.1), N reduces to

$$N = 2 \frac{B_{e}^{*} + 1}{B_{e}^{*}} = (2 + y_{e}^{*} - 1) = 2 + 1$$
(B. 17)

Substituting Eqs. (B. 15), (B. 16), (B. 17) in the various equations giving the velocity components, sonic line, line of horizontal velocity and the limiting characteristics, the similarities may be noted.

APPENDIX C

Existence of a Velocity Potential

For small deviations from equilibrium of a reacting gas flow, the flow may be assumed to be nearly isentropic, giving rise to the existence of a velocity potential. This may be shown as follows:

The entropy equation for reacting gas flows is given by (Refs. 6, 9)

$$T \operatorname{grad} S = \operatorname{grad} h - \frac{1}{b} \operatorname{grad} p + \operatorname{Q} \operatorname{grad} \alpha$$
 (C1)

where T, S, h, ρ , p are temperature, entropy, enthalpy, density and pressure respectively, α is the atomic mass fraction and Q is the difference between the specific chemical potential of atoms and molecules given by (Ref. 5)

$$Q = RT \log \left[\frac{2 e_d}{e} \left(\frac{T}{\theta_v} \right)^{1/2} e^{-\theta_d/T} \left(1 - e^{-\theta_v/T} \right) \left(\frac{1 - \alpha}{\alpha^2} \right) \right]$$
 (C2)

where is is the characteristic dissociation density, θ_v , θ_d are characteristic temperatures for vibration and dissociation, respectively, and R is the gas constant per unit mass referred to the diatomic gas. In terms of the local equilibrium value of α_e , Q takes the form

$$Q = RT \log \left[\frac{\alpha_e^2}{1 - \alpha_e} \cdot \frac{1 - \alpha}{\alpha^2} \right]$$
 (C3)

By Scalar multiplication of Eq. (C1) by \vec{q} , one obtains the variation of entropy along a streamline as

$$T\vec{q} \cdot grad S = T \frac{DS}{Dt} = Q\vec{q} \cdot grad \alpha = Q \frac{D\alpha}{Dt}$$
 (C4)

Since from the energy equation Eq. (9), $\frac{Dh}{Dt} - \frac{1}{2} \frac{Dp}{Dt} = 0$, where, $\frac{D}{Dt} = \vec{q} \cdot 8 \text{ rad}$, Eq. (C4) may be written using streamwise coordinate s as

$$\frac{\partial S}{\partial s} = \frac{Q}{T} \frac{\partial \alpha}{\partial s} \tag{C5}$$

$$= R \log \left[\frac{\alpha_e^2}{1 - \alpha_e} \cdot \frac{1 - \alpha}{\alpha^2} \right] \frac{\partial \alpha}{\partial 5}$$
 (C6)

$$\alpha = \alpha_* \left(1 + \Upsilon \alpha' \right) \tag{C7}$$

$$\alpha_e = \alpha_* \left(1 + \Upsilon \alpha_e' \right) \tag{C8}$$

so that α' and α'_e are of order unity.

Then $d\alpha = \alpha_* \Upsilon d\alpha' \qquad (C9)$ and $\frac{\alpha_e^2}{1-\alpha_e} \cdot \frac{1-\alpha}{\alpha^2} = \frac{\alpha_*^2 \left(1+\Upsilon \alpha_e'\right)^2}{\left(1-\alpha_*\right)\left(1-\frac{\Upsilon \alpha_* \alpha_e'}{1-\alpha_*}\right)} \cdot \frac{\left(1-\alpha_*\right)\left(1-\frac{\Upsilon \alpha_* \alpha_e'}{1-\alpha_*}\right)}{\alpha_*^2 \left(1+\Upsilon \alpha'\right)^2}$ $= \left[1+2\Upsilon \alpha_e' + o(\Upsilon^2)\right] \left[1-2\Upsilon \alpha' + o(\Upsilon^2)\right] \left[1+\frac{\Upsilon \alpha_* \alpha_e'}{1-\alpha_*} + o(\Upsilon^2)\right]$ $\left(1-\frac{\Upsilon \alpha_* \alpha'}{1-\alpha_*}\right)$ $= \left[1+\Upsilon \left(2\alpha_e' - 2\alpha' + \frac{\alpha_* \alpha_e'}{1-\alpha_*} - \frac{\alpha_* \alpha'}{1-\alpha_*}\right) + o(\Upsilon^2)\right]$

$$= \left[1 + \Upsilon \left(\alpha_{\bullet}' - \alpha'\right) \left(2 + \frac{\alpha_{+}}{1 - \alpha_{+}}\right) + O\left(\Upsilon^{2}\right)\right]$$

$$= \left[1 + \Upsilon(\alpha'_{\bullet} - \alpha')\left(\frac{2 - \alpha_{\bullet}}{1 - \alpha_{\bullet}}\right) + O(\Upsilon^{2})\right] \tag{C10}$$

and

$$\log\left[\frac{\alpha_e^2}{1-\alpha_e},\frac{1-\alpha}{\alpha^2}\right] = \Upsilon\left(\alpha_e' - \alpha'\right)\left(\frac{2-\alpha_*}{1-\alpha_*}\right) + O(\Upsilon^2) \tag{C11}$$

by series expansion. Thus the change in entropy dS along a streamline is obtained as (multiplying by ds on both side of (C6))

$$d(5/R) = \Upsilon^2 \frac{\alpha_*(2-\alpha_*)}{(1-\alpha_*)} (\alpha_*' - \alpha') d\alpha' = O(\Upsilon^2)$$
 (C12)

which shows that the entropy change along a streamline is of order Υ^2 for deviation of α from α_* of order Υ as long as $1-\alpha_*=0(1)$ while for $1-\alpha_*=0(\Upsilon)$

$$d(5/R) = o(7) \tag{C13}$$

Thus for $1-\alpha=0(1)$ and for small deviations from equilibrium, the flow may be considered to be nearly isentropic and hence a velocity potential may be introduced.

Transonic Approximation

In simplifying Eq. (19) or Eq. (21) in the Sonic region, a transformation of the coordinates, Eq. (38) is introduced wherein the y coordinate is distorted by $\Upsilon^{1/2}$ while x is not. The reason for doing so and the relation of Υ to the physical quantities of flow will be considered here.

Let us write the velocity $\vec{\mathbf{q}}$ as a perturbation from the reference state velocity $\vec{\mathbf{q}}$ so that

$$q_{x} = q^{*}(1 + Tu')$$
 (C14)

$$q_{a} = q^{*} \Upsilon U' \qquad (C15)$$

where Υ is of the order of the velocity perturbation from Q^* and U' and U' are of order unity, similarly let

$$\begin{aligned}
\varrho &= \varrho^* (1 + \Upsilon \varrho') \\
\Upsilon &= \Upsilon^* (1 + \Upsilon \Upsilon) \\
\alpha &= \alpha^* (1 + \Upsilon \alpha')
\end{aligned} (C16)$$

Then ho, ha, Man may be written as

$$h_{e} = h_{e^{+}} (1 + \tau h_{e^{+}})$$

$$h_{u} = h_{u^{+}} (1 + \tau h_{u^{+}})$$
(C17)

so that
$$\frac{\theta h_{\theta}}{h_{\alpha}} = \frac{\theta^* h_{\theta^*}}{h_{\alpha^*}} \frac{(1+\tau \theta')(1+\tau h_{\theta'})}{(1+\tau h_{\alpha'})} = \frac{\theta^* h_{\theta^*}}{h_{\alpha^*}} \left[1+\tau (\theta'+h_{\theta'}-h_{\alpha'}) + O(\tau^2) \right]$$

$$\frac{eh_{r}}{h_{r}} = \frac{eh_{r}}{h_{r}} \left(1 + \Upsilon R'_{r} \right) \tag{C18}$$

where
$$R'_{i} = \varrho' + h_{\varrho'} - h_{\alpha'}$$
 (C19)

Similarly

$$\approx \frac{e^{*}(h_{e^{*}} + h_{w^{*}} \alpha_{e^{*}})}{h_{w^{*}}} (1 + T R_{2}')$$
 (C26)

where
$$R'_2 = e' + \frac{h_{e^*}(h_{e^*} - h_{\alpha^*}) + h_{\alpha^*} \alpha_{ee^*} \alpha_{ee^*}}{h_{e^*} + h_{\alpha^*} \alpha_{ee^*}}$$
 (C21)

For the velocity terms,

$$\operatorname{div} \vec{q} = q^* \left[\frac{\partial}{\partial x} (1 + \Upsilon u') + \frac{\partial}{\partial y} (\Upsilon u') \right] = q^* \Upsilon \left(\frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} \right) \quad (C22)$$

$$\begin{split} \frac{D}{Dt} (q^{2}/2) &= (\vec{q} \cdot grad) \frac{q^{*2}}{2} \left[1 + 2 \tau u' + \tau^{2} (u'^{2} + v'^{2}) \right] \\ &= q^{*} \left[(1 + \tau u') \frac{\partial}{\partial x} + \tau v' \frac{\partial}{\partial y} \right] \frac{q^{*2}}{2} \left[1 + 2 \tau u' + \tau^{2} (u'^{2} + v'^{2}) \right] \\ &= \frac{q^{*3}}{2} \left\{ (1 + \tau u') \left[2 \tau \frac{\partial u'}{\partial x'} + 2 \tau^{2} (u' \frac{\partial u'}{\partial x'} + v' \frac{\partial}{\partial y'}) \right] + 2 \tau^{2} v' \frac{\partial u'}{\partial y} \\ &\quad + 2 \tau^{3} v' \left(u' \frac{\partial u'}{\partial y} + v' \frac{\partial}{\partial y'} \right) \right\} \\ &= \frac{q^{*3}}{2} \left\{ 2 \tau \frac{\partial u'}{\partial x'} + 2 \tau^{2} \left[2 u' \frac{\partial u'}{\partial x'} + v' \left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial y'} \right) \right] + \tau^{3} \left(u' \frac{\partial}{\partial x} + v' \frac{\partial}{\partial y} \right) \left(u'^{2} + v'^{2} \right) \right\} \\ &= q^{*3} \left\{ \tau \frac{\partial u'}{\partial x'} + \tau^{2} \left[2 u' \frac{\partial u'}{\partial x'} + v' \left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial y'} \right) \right] + \tau^{3} \left(u' \frac{\partial}{\partial x} + v' \frac{\partial}{\partial y} \right) \left(u'^{2} + v'^{2} \right) \right\} \end{split}$$
From Eq. (28) in the main text

From Eq. (28) in the main text

$$q^{2} + A \alpha_{f}^{2} = q^{*2} + A^{*} \alpha_{f}^{*2}$$

$$\alpha_{f}^{2} = \frac{q^{*2} - q^{2} + A^{*} \alpha_{f}^{*2}}{\Delta}$$
(C24)

or

as shown in Appendix A,

$$A = A^* (I + \Upsilon A')$$

so that

$$\alpha_{4}^{2} = \frac{q^{*2} \left[1 - \left(1 + \Upsilon u' \right)^{2} - \Upsilon^{2} \sigma'^{2} \right] + A^{*} \alpha_{4}^{*2}}{A^{*} \left(1 + \Upsilon A' \right)}$$

$$\approx \alpha_{4}^{*2} \left(1 - \Upsilon A' \right) - q^{*2} \left(2 \Upsilon u' + \Upsilon^{2} u'^{2} + \Upsilon^{2} \sigma'^{2} \right)$$

$$\approx \alpha_t^{+2} \left[1 - \mathcal{T} \left(\Delta' + 2 M_t^{+2} U' \right) + o \left(\mathcal{T}^2 \right) \right]$$
 (C25)

Similarly,
$$q^2 + B \alpha_e^2 = q^{*2} + B^* \alpha_e^{*2}$$
 (C26)

so that
$$\alpha_e^2 \approx \alpha_e^{*2} \left[1 - \Upsilon \left(B' + 2 M_e^{*2} U' \right) + O(\Upsilon^2) \right]$$
 (C27)

Substituting these results in Eq. (19) and writing $\frac{\mathbf{q}^*}{\mathbf{q}^*} = \mathbf{M}^*_{\mathbf{q}}$ and $\frac{\mathbf{q}^*}{\mathbf{q}^*} = \mathbf{M}^*_{\mathbf{q}}$, one has

$$q^{*}\left\{(1+\tau u')\frac{\partial}{\partial x} + \tau u'\frac{\partial}{\partial y}\right\} \frac{\ell^{*}h_{\ell^{*}}}{h_{\alpha^{*}}}(1+\tau R_{1})\left[q^{*}\tau(\frac{\partial u'}{\partial x} + \frac{\partial u'}{\partial y})\right] - q^{*}M_{f}^{*2}\left\{\tau \frac{\partial u'}{\partial x} + o(\tau^{2})\right\} = \frac{\Psi_{*}L_{\alpha^{*}}\ell^{*}(h_{\ell^{*}} + h_{\alpha^{*}}\alpha_{e\ell^{*}})}{h_{\alpha^{*}}}(1+\tau R_{2}) - q^{*}M_{e}^{*2}\left\{\tau \frac{\partial u'}{\partial x} + o(\tau^{2})\right\}$$
(C28)

Keeping the lowest order terms in Υ on the LHS and all others on the right hand side, and dividing throughout by $Q^{*2}Q^*h_{Q}^*$ and writing $\beta = \frac{K_*}{Q_*^*}$ where

$$K_* = \frac{\Psi_* L_{\alpha^*} \left(h_{e^*} + h_{\alpha^*} d_{ee^*} \right)}{h_{e^*}} \qquad h_{\alpha^*} \qquad (C29)$$
one obtains

$$\frac{\partial^{2}}{\partial x} \left\{ \Upsilon (1 - M_{t}^{*2}) \frac{\partial u'}{\partial x} + \Upsilon \frac{\partial u'}{\partial y} \right\} - \beta \Upsilon \left\{ \frac{\partial u'}{\partial x} (1 - M_{e}^{*2}) + \frac{\partial u'}{\partial y} \right\} =$$

$$- \Upsilon^{2} \left[u' \frac{\partial}{\partial x} + u' \frac{\partial}{\partial y} \right] \left[(1 - M_{t}^{*2}) \frac{\partial u'}{\partial x} + \frac{\partial u'}{\partial y} \right] + \beta \Upsilon^{2} M_{e}^{*2} \left[2 u' \frac{\partial u'}{\partial x} + u' (\frac{\partial u'}{\partial x} + \frac{\partial u'}{\partial y}) \right]$$

$$+ \beta \Upsilon^{2} R_{2} \left[(1 - M_{e}^{*2}) \frac{\partial u'}{\partial x} + \frac{\partial u'}{\partial y} \right] + O \left(\Upsilon^{3} \right)$$

$$+ \beta \Upsilon^{2} R_{2} \left[(1 - M_{e}^{*2}) \frac{\partial u'}{\partial x} + \frac{\partial u'}{\partial y} \right] + O \left(\Upsilon^{3} \right)$$

$$(C30)$$

Introducing the perturbation velocity potential ϕ , such that

$$u' = \Phi_{x} \quad , \quad \sigma' = \Phi_{r} \tag{C31}$$

and the transformation

$$\chi = \beta \chi \qquad (C32)$$

$$\eta = \beta \sqrt{1 - M_f^{*2}} y$$

$$\bar{\Phi}(\xi, \eta) = \beta \Phi(x, y)$$

where, β is given in Eq. (C29) and $1/\beta$ has the dimensions of length. Then,

$$\frac{\partial \hat{A}}{\partial n_{i}} = \frac{\partial \hat{$$

Substituting these in Eq. (C30), and simplifying

$$\begin{split} \beta^{2} \Upsilon(1-M_{+}^{*2}) \Big\{ \frac{\partial}{\partial E} (\bar{\Phi}_{EE} + \bar{\Phi}_{\eta \eta}) - \left[\frac{1-M_{e}^{*2}}{1-M_{+}^{*2}} \bar{\Phi}_{EE} + \bar{\Phi}_{\eta \eta} \right] \Big\} = \\ -\beta^{2} \Upsilon^{2} (1-M_{+}^{*2}) \Big[\bar{\Phi}_{E} \frac{\partial}{\partial E} + \sqrt{1-M_{+}^{*2}} \bar{\Phi}_{\eta} \frac{\partial}{\partial \eta} \Big] (\bar{\Phi}_{EE} + \bar{\Phi}_{\eta \eta}) - \beta^{2} \Upsilon^{2} (1-M_{+}^{*2}) \\ \frac{\partial}{\partial E} \Big[R_{1} (\bar{\Phi}_{EE} + \bar{\Phi}_{\eta \eta}) \Big] - 2\beta^{2} \Upsilon^{2} M_{+}^{*2} \frac{\partial}{\partial E} \Big[\bar{\Phi}_{E} \bar{\Phi}_{EE} + (1-M_{+}^{*2}) \bar{\Phi}_{\eta} \bar{\Phi}_{E\eta} \Big] \\ + 2\beta^{2} \Upsilon^{2} M_{e}^{*2} \Big[\bar{\Phi}_{E} \bar{\Phi}_{EE} + (1-M_{+}^{*2}) \bar{\Phi}_{\eta} \bar{\Phi}_{E\eta} \Big] \\ + \beta^{2} \Upsilon^{2} (1-M_{+}^{*2}) R_{2} \Big[\frac{1-M_{e}^{*2}}{1-M_{+}^{*2}} \bar{\Phi}_{EE} + \bar{\Phi}_{\eta \eta} \Big] + O(\Upsilon^{3}) \end{split}$$
(C34)

what is essentially achieved by this transformation is as follows. In the linerised treatment of Vincenti (Ref. 6) the terms on the LHS of Eq. (C30) or

Eq. (C34) are kept. Thus comparing the various terms on the LHS,

$$\frac{\partial}{\partial \varepsilon} (\bar{\Phi}_{\eta \eta}) = O(\bar{\Phi}_{\eta \eta}) \quad \text{or} \quad \varepsilon = O(1)$$
 (C35)

$$\frac{\partial}{\partial E}(\bar{\Phi}_{EE}) = O\left[\frac{1 - M_e^{*2}}{1 - M_+^{*2}}\bar{\Phi}_{EE}\right] \quad \text{or} \quad \frac{1 - M_+^{*2}}{1 - M_e^{*2}} = O(E) = O(I) \quad \text{(C36)}$$

Also
$$\bar{\Phi}_{\epsilon\epsilon} = O(\bar{\Phi}_{\eta\eta})$$
 or $\bar{\Phi}_{\eta} = O(\eta \bar{\Phi}_{\epsilon})$ (C37)

Furthermore, the terms on RHS should be of a higher order compared to the terms on LHS. It may be noted that all the terms on RHS contain β^2 as do those on the LHS. However, not all of the terms on the RHS contain $(I-M_{+}^{*2})$ which appears on LHS. Also terms on the RHS containing $(I-M_{+}^{*2})$ are already of order Υ^2 while the LHS terms of order Υ . So the only terms to be compared are those which do not contain $(I-M_{+}^{*2})$. Thus comparing these with the first term on the LHS gives the conditions for the linearisation to be valid, namely

$$\frac{2\beta^{2}\Upsilon^{2}M_{e}^{*2}\bar{\Phi}_{e}\bar{\Phi}_{e}\bar{\Phi}_{e}}{\beta^{2}\Upsilon(1-M_{f}^{*2})\bar{\Phi}_{egg}} \ll 1$$
 (C38)

$$\frac{2 \beta^2 \Upsilon^2 M_t^{*2} \overline{\Phi_{\epsilon} \Phi_{\epsilon \epsilon \epsilon}}}{\beta^2 \Upsilon (1 - M_t^{*2}) \overline{\Phi_{\epsilon \epsilon \epsilon}}} \ll 1$$
(C39)

$$\frac{2\beta^{2}\Upsilon^{2}M_{+}^{*2}\overline{\Phi_{\xi\xi}^{2}}}{\beta^{2}\Upsilon(1-M_{+}^{*2})\overline{\Phi_{\xi\xi\xi}}} \ll 1$$
 (C40)

Since $\xi = O(1) \overline{\Phi_{e \pm e}} = O(\overline{\Phi_{e \pm}}) = O(\overline{\Phi_{e}})$ and also $M_{e}^{*2} = O(M_{e}^{*2})$ thus all the conditions (C38) to (C40) simplify to the single condition

$$\frac{2 T M_f^{*2} \bar{\Phi}_{\sharp}}{(1 - M_f^{*2})} < 1 \tag{C41}$$

since Φ_{t} is independent of Υ and $(I-M_{t}^{*2})$ this condition may be satisfied as long as $I-M_{t}^{*2}=O(I)$ or $O(\Upsilon^{1/2})$. But as soon as $I-M_{t}^{*2}=O(\Upsilon)$, this condition may not be satisfied and one will have to keep the three terms containing M_{t}^{*2} , M_{e}^{*2} in the RHS of Eq. (C34).

The perturbation parameter au may be related to the physics

of the flow as follows:

Let h = f(x) describe the shape of a nozzle in the vicinity of the geometrical throat, the x-axis is along the nozzle cexterline and the origin at the throat.

^ y

Let h_o be the semi-height at the throat. Then expanding f(x) in a Taylor series about x = 0

$$h = f(0) + x f'(0) + \frac{x^2}{2} f''(0) + \frac{x^3}{6} f''(0) + \frac{x^4}{24} f''(0) + \cdots$$
 (C42)

For h symmetric with respect to y-axis, $f(o)=h_o$, f(o), f(o)=0 and $f(o)=1/R_o$ where Ro is the radius of curvature at the throat. Also Hall (Ref. 12) gives $f_{(0)}^{(0)} = 30/R_{\bullet}^{(0)}$ with 0 = 1, 0, -1 for parabolic, circular arc, and hyperbolic nozzle shapes. Thus for these shapes

$$\frac{h}{h_0} = 1 + \frac{x^2}{2h_0R_0} + \frac{\sigma x^3}{8h_0R_0^3} + \cdots$$
 (C43)

The boundary condition on the nozzle wall (flow tangency) gives

$$q_y/q_x = \frac{dh}{dx}$$
 at $y = h$ (C44)

i.e.,
$$\tau \sqrt{1 - M_{+}^{*2}} \Phi_{\eta} = \tau \Phi_{\tau} = (1 + \tau \Phi_{x}) \left[\frac{\epsilon}{h \cdot \beta} \epsilon + \left(\frac{\epsilon}{h \cdot \beta} \right)^{3} \frac{\sigma}{2} \epsilon^{3} + \cdots \right]$$

at $\eta = h_{o} \beta \sqrt{1 - M_{+}^{*2}} \left[1 + \left(\frac{\epsilon}{h \cdot \beta} \right)^{2} \epsilon + \cdots \right]$

(C45)

where $\varepsilon = h_0/R_0$ For small &, one has

$$\tau \sqrt{1-M_{+}^{*2}} \overline{\Phi}_{\eta} \approx \frac{\epsilon}{h_{0} \beta}$$
 at $\eta \approx h_{0} \beta \sqrt{1-M_{f}^{*2}}$ (C46)

which on substitution in Eq. (C41) shows that the linearisation is valid. In contrast with perfect gas flows where only $\mathbf{E} = \frac{\mathbf{h} \cdot \mathbf{e}}{2}$ has to behave as $(\mathbf{I} - \mathbf{M}_{\mathbf{f}}^{*2})^2$ as $(\mathbf{I} - \mathbf{M}_{\mathbf{f}}^{*2})^2$, bringing in the characteristic dissociation relaxation length \mathbf{I}/\mathbf{p} non-dimensionalised by the nozzle semi-height $\mathbf{h}_{\mathbf{e}}$.

In other words, the linearised treatment can be valid if the thickness parameter & behaves as

$$\frac{\varepsilon}{h_0 \beta} \sim A \left(1 - M_+^{*2} \right)^{2} \tag{C49}$$

where A is a constant of proportionality i.e. for a given thickness ratio parameter \mathcal{E} if $h_{\bullet}\beta$ behaves as $(1-M_{\bullet}^{-1})^{-2}$ as $M_{\bullet}^{-1} \to 1$, the linearised analysis will still give valid results i.e.

 $\frac{1}{h_0 \beta} \sim (1 - M_+^{*2})^{2^{1/2}}$ as $M_+^{*} \rightarrow 1$ (C50)

which implies that the dissociational relaxation length $1/\beta$ should be small compared to the tunnel semi-height h_{\bullet} . In other words, for flows very near equilibrium in the throat region such that the dissociational relaxation length is much smaller than the nozzle semi-height the linearised treatment will correctly describe the flow behaviour near the throat. For any other behaviour of $h_{\bullet}\beta$, the linearisation is not valid and one has to keep some of the terms on the RHS of Eq. (C34). Then one will have to choose a suitable relationship between γ and $1-M_{\bullet}^{\bullet 2}$. One such relationship is

$$\Upsilon \sim \left(1 - M_{+}^{*2}\right) \tag{C51}$$

as in perfect gas flows (Ref. 10). With this choice, the transformation ($\mathbb{C}32$) becomes

$$\Xi = \beta \propto \qquad \eta = \beta \Upsilon^{1/2} y$$

$$\overline{\Phi}(\xi, \eta) = \beta \Phi(x, y) \qquad (C52)$$

or choosing h_{ullet} , the tunnel semi-height, as the flow characteristic length, one may write

$$\xi = \frac{\varphi}{h}$$
, $\eta = \frac{\gamma^{1/2} y}{h}$, $\eta = \frac$

which is the same as Eq. (38) in the text.